THE ROLE OF THE COLLECTOR IN FROTH FLOTATION

Being a thesis submitted by

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to the University of Glasgow in fulfilment of the requirements for the Degree of Doctor of Philosophy in Applied Science.

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November, 1950.

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ACKNOWLEDGMENTS.

The author wishes to acknowledge his indebtedness to Professor W.M. Cumming, O.B.E., D.Sc., F.R.I.C., M.I. Chem. E., F.R.S.E., and to Professor P.D. Ritchie, B.Sc., Ph.D., F.R.I.C., for providing all the necessary facilities and for their continued interest in the investigations; to Professor G. Hibberd, Ph.D., A.R.T.C., M.I. Min. E., for his kindness in obtaining the required minerals; to W. Gibb, B.Sc., Ph.D., A.R.T.C., A.R.I.C., for his constant help, guidance and useful criticisms throughout the course of this work; to A.B. Crawford, B.Sc., Ph.D., A.R.T.C., F.R.I.C., for the spectroscopic analyses of the barytes samples; and to T.J. Mitchell, Ph.D.,A.R.T.C., F.R.I.C., A.M.I. Chem. E., for his helpful criticisms.

Thanks are also due to Mr. R. Barbour for making the various glass apparatus, to the Workshop of the Technical Chemistry Department for the Permeability Cells used for surface area measurements, to Mr. J. Donald of the Geography Department, Glasgow University, for the micro-photographs of barytes powders, and finally to the Government of the Union of Burma for the award of the scholarship which made this research possible.

C O N T E N T S.

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Summary of Thesis.

The importance of the polar-non-polar structure in the collector molecule is explained and a review is made of the present state of knowledge regarding the mechanism of collection in froth flotation. Using the bubble column, the froth stabilities of the lower fatty acids, which possess low collecting power, are compared and the results discussed with respect to the concentration at the air-liquid interface. Preliminary flotation tests are carried out on the variation in recovery of barytes with time of collection, rate of air flow, pulp density, and particles size, in a laboratory flotation cell to obtain the optimum conditions for later experiments. Tests on flotation of purified natural barytes with fatty acids and sodium soaps indicate that a complete monolayer of the collector is not necessary for maximum flotation and that adsorption of acid anion and not the formation of barium salt of the acid is responsible for collection. Physical adsorption of the fatty acid anion takes place with the hydrogen ions as counter ions. The effect of pH on flotation with caprylic acid, sodium caprylace, and lauric acid, is studied. The presence of the anions, hydroxyl, carbonate, and sulphate ions, is found to depress the flotation while the cations, barium ions, bring about activation. Hydrogen and ferric ions, however, depress the flotation. The part played by these ions is discussed. An investigation is made of the adsorption of ferric ions on natural barytes and pure barium sulphate. From the findings, a hypothesis on the mode of the

adsorption and its relation to the depressing action, is put forward. Flotation of pure barium sulphate with sodium laurate is compared with that of natural barytes using the Hallimond Tube. Exploratory tests are done on the adsorption of the lower fatty acids on pyrites, silica, and barytes. The pH and the potentiometric titration methods indicate unimolecular adsorption of these acids on pyrites and barytes. The nitrogen adsorption method, Rigden's water permeability method, and the Lea and Nurse air permeability method are used for measuring the surface areas of the powders tested. The applicability of these three methods to flotation research is discussed.

I N T R O D U C T I O N.

Froth flotation may be defined simply as the science of separating particles from each other in a liquid suspension by means of air bubbles. As implied in this definition, one of the first uses of flotation was to separate 'solids' from 'solids' as in the flotation of useful minerals from the unwanted gangue particles. Now, however, froth flotation is also a recognised process for removing solids from liquids, and research is under way to apply it to the separation and reclamation of liquids from liquids.

Even although ninety years have elapsed since the first patent in 1860 by William Haynes (1), the froth flotation process is still largely an art as far as plant practice is concerned. Empirical research has been largely responsible for its rapid progress to the present stage of application. It was only at the beginning of the present century that attention began to be paid to the fundamental aspects of the process. The present intensive research, being carried out in America and Australia, has helped to make the subject more of a science but a great amount of fundamental work remains to be done on the underlying basic principles.

The realisation that air bubbles may become attached to some minerals and not to others brought about a revolution in flotation research. Investigators at once tried to enhance the differences between the minerals by the empirical method of adding to the pulp any substance in solid,

liquid or gaseous state which might possibly have some effect on the separation. That this trial and error method was successful is evident from the citation of over two thousand flotation reagents in Taggart's Handbook of Ore Dressing (2).

The next notable step forward was the classification of these reagents into different groups according to their functions in flotation. Out of several suggestions made by various authors, the following four are now recognised as the main types used in the process:- frothers, collectors, activators and depressants.

These are defined according to Wark (3) as:-

(1) Frothers:- A "frother" is a substance which, when dissolved in water, enables it to form a more or less stable froth with air.

(2) Collector:- A "collector" for any mineral is a substance (generally organic), which induces it to float at the air-water interface, and in the presence of a frother to form a more or less stable mineralised froth.

(3) Activators:- An "activator" for any mineral is a substance (generally inorganic), the addition of which induces flotation in the presence of some collector that is otherwise without effect on the mineral.

(4) Depressants:- A "depressant" for any mineral is a substance (generally inorganic), the addition of which prevents a collector from functioning as such for that mineral.

The role of the collector is obvious from the above definition. A frother is necessary to provide the large

air-solution interface to which the mineral particles become attached, but a collector must also be there in order that the desired attachment may take place. In other words, the collector molecule acts as a link between the air-bubble and the mineral particle. Thus, the part played by the collector may be likened to that of a chain connection between a carrier vehicle and a trailer. Wark and Cox (4) attributed this action of the collector to the adsorption of the collector molecule at the solid-solution interface with the formation of a monomolecular layer.

To the physical chemist, therefore, froth flotation is a case where two types of surface phenomena are involved in the same system. Frothing is the surface effect of soluble molecules at the liquid-gas interface, while collection is that at the solid-liquid interface. The difficulty of arriving at a definite theory of collection will be realised if one considers the fact that very little is known about the surfaces of solids in contact with liquids. The study of adsorption at the solid-liquid interface is, at the moment, far behind that of adsorption at gas-liquid interface. Although some inferences as to the nature of solid surfaces can be drawn from the gaseous adsorption on solids, the data obtained from such experiments cannot be easily related to the case of adsorption in liquids as the solid surfaces behave differently in the two media. It is, therefore, clear that further advances in physical chemistry of surfaces and molecular physics must be awaited before any flotation theory can be put on a firm theoretical basis. In the meantime flotation

research will have to make use of whatever new techniques and data are available from the related fields such as crystallography, colloid chemistry, and analytical chemistry, in order that tentative theories may be developed.

The problem may be attacked in yet another manner. The number of variables may be reduced to a minimum and the interaction of one homologous series of compounds with one pure mineral be studied under rigid conditions of experiment. Then by introducing variables one at a time the theory of the collector can be built up.

It was decided in this case that the homologous series of monocarboxylic acids, i.e., fatty acids, be studied due to the extensive use of the higher members in flotation practice and to the relative ease with which pure samples of these materials can be obtained.

Of the minerals available in quantity locally, it was soon found that hand-picked samples of practically pure barytes gave the most reproducible results, this being due no doubt to the relative inertness of that material to air and water. This study, therefore, in its later stages, developed into a study of the effect of the fatty acids on the flotation of barytes. The techniques used new, modified, and established are such as can be easily applied to other collector-mineral systems.

COLLECTORS.

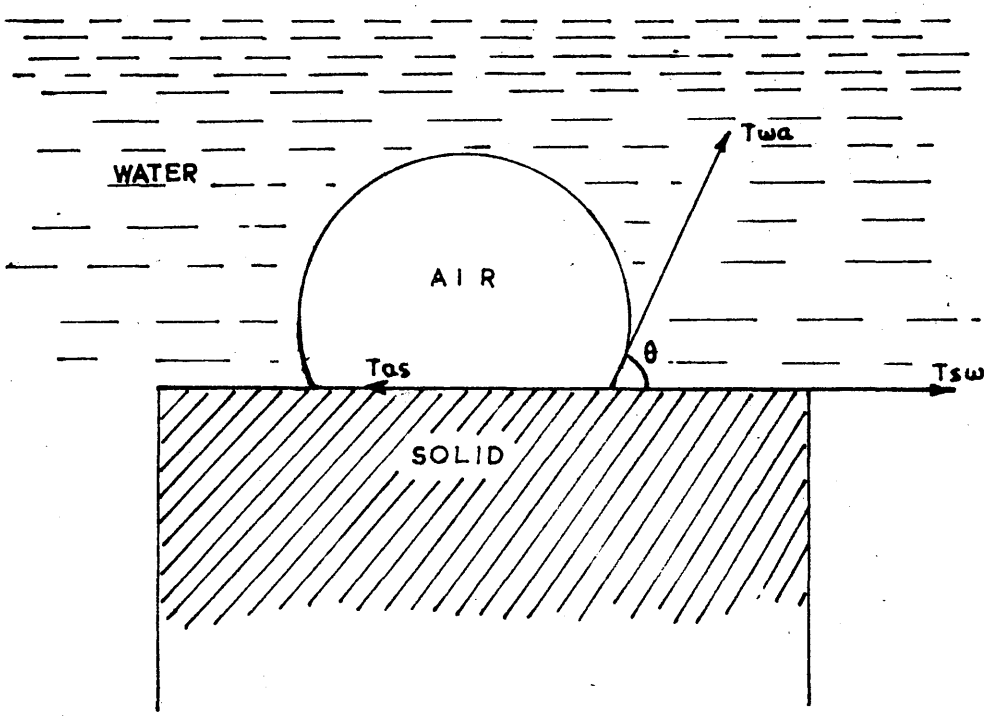
Chapter I.

Role of Collector.

The principle feature of the froth flotation process is the adhesion between a particle of mineral, previously wetted by water, and an air bubble large enough to carry it up to the surface. In practice, the particles are so small compared to the bubbles that many of them become attached to each of the air bubbles. A highly mineralised bubble may even sink to the bottom. At the outset, it should be mentioned that this adhesion between the mineral and the bubble can only be achieved in the presence of a collector. Contact angle measurements with clean mineral surfaces under distilled water gave zero contact angles or, in other words, no sticking between the air bubble and the mineral surface. Contact is obtained immediately on the addition of a collector to water.

Apparently, therefore, the collecting agent performs this most important task of making the mineral surface air-avid and ready for a mineral-bubble attachment. The way in which this takes place was first shown in 1930 by Taggart, Taylor, and Ince (5) who generalised that all soluble collectors possess both a polar or active group and a non-polar or inactive group. The polar group attaches itself to the mineral surface while the non-polar group projects into the air bubble thus forming a connecting link between the mineral

FIG - (1)



EQUILIBRIUM RELATIONSHIP FOR A BUBBLE OF AIR IN CONTACT WITH A MINERAL SURFACE UNDER WATER

and the bubble. This theory was substantiated a year later by Wark and Cox (4) who found that the selective flotation of a particular mineral was based upon the formation of a film of the collector on the surface and not upon the enhancement of the inherent floatability as was thought previously. They not only proved that most minerals have no inherent floatability but also deduced from the contact angles measurements that the film was unimolecular in thickness with the molecules as closely packed as possible.

Wetting and Contact Angle.

Since the ability of a mineral particle to float depends upon whether air can displace water from the surface of the particle, it will be of advantage to consider the physical principles underlying this process. As already stated, the air bubble can only spread upon the mineral surface in the presence of a collector. Even after the formation of a layer of collector over the mineral, displacement of water from the surface by air cannot proceed until a definite contact angle has been established, whose magnitude is determined by the nature of the three interfaces - water-air, air-mineral, and mineral-water. These three interfaces meet along a line of triple contact as shown in Fig. (1).

Let Tas, Tsw and Twa dynes per cm. by the surface tensions at the interfaces air-solid, solid-water, and water-air respectively. These values are numerically equal to the surface energies measured in ergs. per sq. cm.. From the principle of minimum energy, air will not replace water at

the mineral surface unless the sum of all the surface energy terms, after the change, is less than the sum before the change. Again, the creation of an air-mineral interface will mean the destruction of water-air and mineral water interfaces of equal area. The necessary condition for such a change is, therefore, that

$$Tas < Twa + Tsw$$

The work done per unit area by the system during the change is given, in ergs, by -

$$W = Twa + Tsw - Tas \quad \ldots\ldots\ldots\ldots (1)$$

The difficulty in employing this equation for practical purposes lies in the absence of satisfactory methods of determining Tsw and Tas, although Twa can be measured by a number of methods.

This problem was solved by using the conception of contact angles. When the bubble has spread over the surface and has attained the equilibrium state, as in Fig. (1), a definite angle of contact "θ" is formed between the air-water and solid-water interfaces. From the equilibrium of forces,

$$Tas = Twa \cos\theta + Tsw$$

$$\text{or, } Tas - Tsw = Twa \cos\theta \quad \ldots\ldots\ldots\ldots (2)$$

From equations (1) and (2), an equation for the work done by the system is obtained as, -

$$W = Twa\,(1-\cos\theta)$$

The value of W is a measure of the "tenacity of adhesion" between the mineral and air. It is dependent upon the contact angle and, therefore, for a mineral to float the value of θ is important. If $\theta = 0°$, W becomes zero; that

is, there is no mineral-bubble attachment. If θ = 180°, the tenacity of adhesion is a maximum and is equal to 2Twa. The greater the value of θ, the greater will be the tendency of air bubble to spread over the mineral surface. The advantage here is that both Twa and θ can be measured experimentally. W also depends upon Twa; that is, the surface tension of the solution should not be too low since the froth could then become "barren" owing to the decrease in the "tenacity of adhesion". The study of contact angles has now assumed a very significant position in flotation research. Traube and Mishizewa (6) has pointed out the close connection between angle of contact and wetting, adhesion, adsorption, and flotation. Indeed, much of our present knowledge regarding the flotation process was gained from contact angle measurements.

Polar-Non-Polar Structure.

Polarisation in a molecule arises from the displacement of electrons in the direction of the more electronegative atom or group of atoms. The result is that electrical dipoles are produced with the elctrical centre some distance away from the mass centre of the molecule. Since the polarity of the hydrocarbons is very small, the distinct heteropolar character of the organic compounds under discussion must be ascribed to the introduction of polar groups into the hydrocarbon chains.

Evidently, a wide range of chemical reagents can be made available for use by not only taking different hydrocarbon groups, but also by changing the polar end.

The simplest and at the same time the most elastic and comprehensive classification of polar groups are:-

(1) Groups containing O, or S, with or without H.

e.g., C=O, -OH, -SH.

(2) Groups containing N.

e.g., -CN, -CNS, $-NO_2$, $-NH_2$.

(3) Groups containing S and O or P and O.

e.g., $-SO_3H$, $-SO_4H$, $-PO_4H_2$, etc.,

(4) Groups containing halogen.

e.g., Cl,Br,I.

That this particular heteropolar build-up of the collector molecule is essential,is clearly indicated by the loss in collecting power of some reagents on introducing suitable hydrophilic groups in the molecule. For instance, diphenyl thioures, $S=C\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}$, is molecule which is adsorbed with the sulphur atom towards the mineral surface and is a good collector; dioxyphenyl thiourea, $S=C\begin{matrix}NH.C_6H_4OH\\NH.C_6H_4OH\end{matrix}$ being adsorbed in the same manner has no longer any collecting properties.

Again, in the case of fatty acids and their soaps, where the carboxyl radical -COOH or -COONa, forms the polar group, and the other group is represented by the hydrocarbon chain, each of these two groups confers certain characteristic properties of its own on the molecule and it is, therefore, necessary that to understand the properties of the molecule as a whole, the part played by each group will have to be considered separately.

The most notable feature of the hydrocarbon chain is its small affinity for water. The longer it is the lower will be the solubility of the compound. Consequently, we find that formic, acetic, propionic, and butyric acids are miscible in all proportion with water, that valeric acid is only moderately soluble, that the next two or three members are very slightly soluble, and that still higher members are described as being "insoluble". Such a gradation in solubility is also exhibited by the soaps. Thus the soluble nature imparted by the carboxyl group is being gradually suppressed by the opposing effect of the hydrocarbon chain.

Similar effects can be brought about by keeping the hydrocarbon chain constant and varying the polar group. For instance, by the introduction of a strong solubilising group such as $-SO_2.OH$ or $-O.SO_2.OH$. or by combining less hydrophilic groups,as in amides and sulphonides, the solubility of the molecule can be increased as desired. An obvious properly of the molecule controlled by the polar end is the acidity or alkalinity. A sulphonic group can impart acid property whereas an amino group can give basic property.

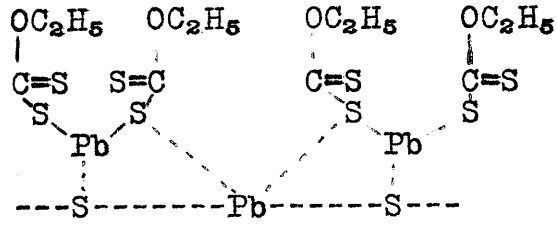
This conflict between the two groups manifests itself in other properties of the molecule associated with surface activity. For example, surface tension, frothing, wetting and detergency are all influenced by these two groups and they, in turn, are related to flotation. When a surface active agent is dissolved in water, the polar end tries to remain in water while the hydrocarbon group is being attracted

towards air and the result is that the molecules arrange themselves on the surface in such a way that the hydrocarbon radical projects out into the air with the polar end dipping in the water. As a consequence, there is an excess concentration of the solute molecules at the water surface as predicted by Gibbs' Adsorption Equation (p. 38). The greater the length of the hydrocarbon chain the more pronounced is this tendency. Thus, the frothing power of the fatty acid solutions and the effect on surface tension of water has been found to increase with the number of carbon atoms.

It may be questioned as to why the frothing agents behave differently from the collecting agents although they possess similar structures. The difference, however, lies in the fact that whereas the polar group of the collector molecule has a greater affinity for mineral surface, the polar group of the frother molecule has a greater affinity for water. Since the fatty acids and their soaps can act as frothers as well as collectors, it seems that the carboxyl radical has, in some cases, an almost equal attraction for water and mineral surfaces.

The activity of the molecule as a collector is, of course, due to the polar group. It was, in fact, because of the reactive nature of these groups that the "Reaction Theory of Collection" was put forward by Taggart and his colleagues (5). To quote two examples, first take the case of potassium ethyl xanthate and galena. That galena is very easily oxidised by atmospheric oxygen is well known.

Taggart and others, therefore, considered that potassium ethyl xanthate reacts with lead sulphate on the surface of galena forming lead ethyl xanthate, as shown below, since they could extract this compound by leaching with alcohol.



Diphenyl thiourea, $S = C \begin{matrix} NH \cdot C_6H_5 \\ NH \cdot C_6H_5 \end{matrix}$, is another case in which a lead compound was extracted from aqueous solution.

The study of the effect of various polar and non-polar radicals on surface activity and allied phenomena, and the development of new reagents has now more or less passed into the hands of detergent chemists since the detergency industry uses a wider range of these chemicals than the metallurgical.

Classification of Collectors.

The collectors are classified into "ionic" and "non-ionic" types; the former are sub-divided into 'anionic' and 'cationic' groups.

The 'anionic' collectors are those compounds which give rise to anions containing the hydrocarbon group. They include the organic acids and their sodium and potassium salts. Fatty acids and their soaps are common examples with the hydrocarbon chain contained in the anion, $R.COO^-$. Belonging to this class, the xanthates are the most widely used of all collectors. They are of the general formula, $R\text{-}O\text{-}C \begin{matrix} S \\ SM \end{matrix}$,

where R and M represent the hydrocarbon chain and metallic atom respectively. Other compounds such as thiocarbonate, dithiophosphates, mercaptans, and alkyl sulphonic acids, may be mentioned, but there are too many of them to be dealt with in detail here.

The 'cationic' collectors, which give rise to cations containing the hydrocarbon group, have not been so well exploited as the anionic type. The important members of this class are derivatives of the amines and certain organic analogues of the ammonium salts. Some of the amines themselves are collectors. A good example is the interesting collector, cetyl trimethyl ammonium bromide, $C_{16}H_{33}.N(CH_3)_3.Br$. Aromatic compounds like α-naphthylamine and aniline are also collectors for some minerals.

The 'non-ionic' collectors are also soluble and heteropolar but undoubtedly adsorb as whole molecules (examples are dixanthogen, aliphatic and aromatic sulphides and disulphides, and triphenylphospine) (7).

Oily collectors, such as kerosene and creosote, used to some extent especially in the flotation of oxidised minerals and coal, are not considered here as they act chiefly through the formation of a coating of oil on the mineral surface and to a much lesser extent through chemisorption.

A study of reaction rates in aqueous solution shows that the reactions are quickest in the case of ions and ions, slower between ions and polar molecules, and slowest for polar molecules only. For example, the precipitation of barium

sulphate from barium chloride and sulphuric acid is almost instantaneous. Then, the hydrolysis of polar alkyl acetate, $CH_3.COOR$, by hydroxyl ions of an alkali is a relatively slow reaction. Finally, few reactions are known to take place between weakly dissociated or undissociated molecules, especially in aqueous solution. Most instances cited are those occurring in non-aqueous solvents; e.g.,

$$(C_2H_5)_2S + C_2H_5Br = (C_2H_5)_3S.Br$$

in benzyl alcohol solution.

It is, therefore, clear that for reactions to occur between mineral surface and the heteropolar molecule in so short a conditioning time as 3 to 5 minutes, usually employed in flotation industry, ions must be provided for by either the mineral or the collector or by both.

The problem of the role of the collector now seems to have become a question of whether the ions or the whole molecules are responsible for flotation.

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THEORIES ON COLLECTION.

Chapter II.

Reaction Theory versus Adsorption Theory.

Having found the type of molecules necessary for collecting action in flotation, as already stated, the investigators proceeded to develop a theory for the mechanism of collection and subsequently of activation and depression too. One of the early theories, based on the heteropolar nature of the collector molecule, took into account the complete ionisation of soluble collectors in dilute solutions. The adsorption of these ions was supposed to alter the electrical potential of the mineral surfaces. The minute bubbles formed within the pulp are also electrically charged and it was, therefore, suggested that the mineral-bubble attachment was caused by the presence of opposite charges on the air bubbles and mineral surfaces. Electrical forces, undoubtedly, are involved in assfar as the surface forces are concerned but the theory, in this simple form, has not been generally accepted.

Out of all the many theories put forward only two have stood the test of time. One is the "Chemical Reaction Theory" of Taggart and his co-workers and the other is the "Adsorption Theory" of Wark and Cox. A great deal of work has been done and much experimental evidence has been cited in favour of each theory but the controversy, at the moment, is still unsettled.

Considering first the Chemical Reaction Theory,

Taggart, Taylor and Knoll (8) in 1930 made a generalisation applicable to all soluble collectors, activators and depressants. The essence of it is, to quote their own words, that "All dissolved reagents, which, in flotation pulps, either by action on the to-be-flotated or on the not-to-be-floated particles affect their floatability, function by reason of chemical reactions of well-recognised types between the reagent and the particle affected."

In support, they quoted the first case of chemical reaction in flotation. It was the activation of sphalerite by copper sulphate which was discovered by Gates and Jacobsen (9) to take place according to the following reaction:-

$$CuSO_4 + ZnS \rightarrow ZnSO_4 + CuS$$

Their main experimental proof was centred around the reaction of xanthated on galena and sphalerite. They showed that these two sulphides were first oxidised to sulphate which then reacted with xanthate by double decomposition. The result was the formation of a coating of a relatively insoluble salt of the base-metal cation with organic anion at the mineral surface.

Further work on this subject was done by Knoll (10) and also by Taylor and Knoll (11) who made a detailed study of the reactions between powdered galena and potassium ethyl xanthate solutions. A complete stoichiometric relation was found to exist between the xanthate ion abstracted from solution and sulphate plus sulphoxide ions thrown into solution. The concentration of the original potassium ethyl xanthate solution was 16.3 mg. per litre, or less, which was of the

order of concentration of the collector solutions usually employed in flotation. With higher concentrations of xanthate more xanthate ion was removed but a stoichiometric amount of carbonate ion went into solution. This exchange of xanthate and carbonate ions increased with increasing xanthate concentration until all the carbonate present in the original galena had gone into solution.

Similar experiments were performed by Gaudin and his co-workers (12) using galena, chalcocite and covellite. They found that the oxidised coatings of galena react metathetically with potassium xanthate in solution in water to produce coatings of lead xanthate. Chalcocite and covellite also gave cuprous xanthate with potassium xanthate or dixanthogen. They were, therefore, convinced that the idea of adsorbed reversible coatings does not hold with regard to the sulphide surfaces.

As for the non-sulphide ores, Taggart, Taylor and Knoll cited the work of Luyken and Bierbrauer (13) on the flotation of apatite by sodium palmitate. By measuring pH of the soap solutions, these authors proved that apatite removed sodium palmitate from its aqueous solution and they also postulated that the removal was due to a reaction between the calcium ions of apatite and the anions of soap to form relatively insoluble calcium palmitate at the surfaces of apatite particles. Using galena instead of apatite, they were able to recover palmitate ion far in excess of sodium ion, from the galena. Their conclusion was that sodium

palmitate was not abstracted as such, but that a reaction took place resulting in the production of lead palmitate.

Verification of Luyken and Bierbrauers' work was carried out by Taggart, del Guidice and Ziehl (14). They took a 1:3 pulp containing galena and sodium oleate. After shaking it intermittently for one hour, it was allowed to settle and then elutriated. The solution was decanted free from slimes and free precipitated soap. A known volume of the decanted pulp liquor was acidified with concentrated hydrochloric acid and the liberated oleic acid was determined by extracting with ether and evaporating it to dryness in a tared beaker. Another volume of the liquid was analysed for sodium by a modification of the sodium zinc uranyl acetate method. Finally, the washed galena was treated with a dilute solution of hydrochloric acid and the oleic acid was extracted with ether as before. Sodium content in this case was also determined. Their results showed that oleate ion was removed by the galena while sodium ions remained as they were. They also observed abstraction of oleate ion with calcite and apatite but not with quartz. It may, however, be remarked that their results are rather inconclusive as they produced only two experiments in which the quantities of sodium and oleate ions involved are very small and the experimental errors are large.

Lastly, Taggart and his colleagues mentioned the precipitation reactions with a few of the well-known collectors both acidic and basic and metallic radicals picked at random. They added solutions of potassium ethyl xanthate, thiocarbanilid,

β-naphthylamine, amyl-, heptyl- and benzyl mercaptans and thiocresol to solutions of common metals such as lead, iron and zinc, and showed that precipitates were produced in all the cases examined. Hence they concluded that chemical reactions invariably took place between the collectors and the metallic ions of the mineral surface.

To Taggart and his supporters the word 'adsorption', when applied to flotation has no meaning except that it denotes a concentration difference and nothing more. Where the collector is ionised and hydration of the ions occurs, it would appear to indicate that the affinity of the water for the hydrated ion is greater than that between the two ions of opposite charge. Therefore, it seems to the Taggart school of thought that unless the ion is completely changed by adsorption, it must retain its water-avid character even after adsorption. Consequently they found it difficult to understand how the surface on which the ion was adsorbed, without any reaction, could be imparted a water-repellent nature.

The most recent support for the reaction theory comes from Taggart and Hassialis (15) who studied the relation between solubility product and bubble attachment in flotation. From the results, they postulated that all conditioning and collecting reactions involving ions are predictable on the basis of the solubility product of the least soluble compound involved in the reaction.

The case against the 'Reaction Theory' was presented by Wark and Cox (16). They contended that the reactions

quoted by Taggart, del Guidice and Ziehl could be cases of exchange adsorption, but they did not actually say that the reactions were impossible. The similarity between these two phenomena lies in the fact that an ion from the lattice enters the solution for every ion adsorbed. The distinguishing features, however, are:-

1) ... Whereas the ionic concentrations of the metal and collector in solution need to be high enough to exceed the solubility product for double decomposition, exchange adsorption takes place at lower concentrations.

2) ... The double decomposition reaction usually does not stop at the completion of a monolecular film on the solid surface although the surface coating may sometimes prevent further action.

One example given was the discovery by Paneth and Horovitz (17) that barium sulphate and barium chromate adsorb only those radioactive elements that form highly insoluble sulphates and chromates. Again, silver chloride and chromic oxide do not adsorb radium whose chloride and oxide are fairly soluble. Freundlich pointed out that where adsorption occurred the concentration of the radioactive element was so small that the solubility product of none of its salts could have been exceeded; e.g., radium sulphate cannot exist as such when radium is adsorbed by barium sulphate. Kolthoff and Rosenblum (18) also concluded from their work on the adsorption of dyes on lead sulphate that the reaction is only limited to the surface, as the solubility product of the solid lead Ponceau

salt is not exceeded.

A few of the instances cited were connected with the present work. Gaudin and Hansen (7) found that calcite adsorbs heptoate radicle from solution before any calcium heptoate can be precipitated. The Held and Samochwalov (19) disvoered that laurate ions are adsorbed from sodium laurate solution by barium sulphate. Here the formation of barium laurate by double decomposition is unlikely as barium laurate is more soluble than the sulphate; their solubilities are 0.08 and 0.00023 gms. per 100 gms. of solution (16) respectively. With regard to the last instance, Wark and Cox did not mention the conclusions arrived at by Held and Samochwalov who stated with caution that the first layer on barium sulphate was formed by chemisorption according to the following equation:-

$$BaSO_4 + 2NaL = BaL_2 + Na_2SO_4$$

These authors considered that the possession by the pulp solution of a conductivity greater than that of the original sodium laurate solution was due to the presence of sulphate ions liberated from barium sulphate, for the mobility of SO_4^{--} ion is about four times that of the laurate ion. The analysis of the pulp solution showed the presence of appreciable sulphate ions. They also considered that the formation of a second layer is due to van der Waals forces.

Wark and Cox made some criticisms of some of Taggart's surface coatings as follows. For the flotation of copper minerals, according to Taggart, a coating of copper sulphide was supposed to be first essential so that it may be oxidised to copper sulphate or some other more soluble copper salt.

This copper salt then reacts with xanthate giving a film of copper xanthate. It is difficult to imagine how the soluble copper salt could stay on the surface long enough to react with the xanthate without dissolving in solution. Taggart, del Guidice and Ziehl got over this problem by assuming that the soluble copper salt is held on to the surface by "some tenacious force". As for galena, although its double decomposition with potassium ethyl xanthate is improbable owing to the higher solubility of lead ethyl xanthate, both exchange adsorption and double decomposition are possible for its oxidation product, lead sulphate.

As regards the mechanism of film formation, the problem of flotation of galena by ethyl xanthate and dithiocarbamates were dealt with in detail by Wark and Cox. This is a case where no definite explanation has yet been found in spite of the great amount of work done.

Wark and Cox (20) had shown that galena can be activated by copper sulphate using either sodium aerofloat (sodium diethyl dithiophosphate) or 25 mg./litre potassium ethyl xanthate solution. By analogy with the activation of sphalerite by copper sulphate, they supposed that the reaction is:-

$$PbS + Cu^{++} = Pb^{++} + CuS$$

According to Taggart, however, the reaction should be

$$PbSO_4 + Cu^{++} = Pb^{++} + CuSO_4$$

where $PbSO_4$ is the layer at the surface. Because this reaction is impossible from solubility considerations, Taggart had assumed the absence of $PbSO_4$ at the surface for the time

being.

Next, they found that, using sodium diethyl dithiocarbamate as collector, the quantity of sodium sulphide required to prevent contact at galena surface increases with increase in concentration of the collector. Some sulphide remained in solution throughout these tests. With ethyl xanthate too similar results were obtained and very little sulphide was abstracted by galena. If these observations were to follow Taggart's theory, then no sulphate should be formed on the galena surface owing to the presence of sulphide in solution and consequently no contact should have been obtained. It was, therefore, taken that the collectors were adsorbed directly by galena, as proved by the excellent flotation of galena obtained when 200 mg./l. of either potassium di-n-amyl or n-butyl dithiocarbamate was used in the presence of more than 1 mg./l. sodium sulphide. Although double decomposition may be possible with these two dithiocarbamates, since the solubilities of their lead salts are not known, it cannot be so in the case of di-ethyl- dithiocarbamate. They showed experimentally that its lead salt is more soluble than lead sulphide by adding lead nitrate to a solution containing sodium sulphide and dithiocarbamate, when lead sulphide was precipitated before lead di-ethyl dithiocarbamate.

The above experiments led them to the suggestion that a competitive adsorption at the mineral surface takes place between hydrosulphide (HS^-) and collector ions and that this adsorption may exist even when no soluble sulphide

has been added. There is, of course, a possibility of either a direct adsorption of one or both ions or an exchange adsorption in which the sulphide ions of the lattice takes part in the equilibrium. Which of the two hypotheses hold true could not be verified as difficulties were met with in obtaining pure galena free from oxidised compounds and in detecting or estimating the extremely small quantities involved.

To explain the depressant action of chromates Taggart, del Guidice and Ziehl had stated that chromate ion at the surface cannot be displaced by xanthate ion from solution because the solubility of lead chromate is lower than that of lead xanthate. On the other hand, Knoll (10) found that lead chromate abstracts ethyl xanthate from solution with an equivalent amount of chromate ion passing into solution. Wark and Cox, however, showed that crocoite, the naturally occurring lead chromate, could be floated by high concentrations of ethyl xanthate. The results were reproducible with synthetic fused lead chromate thus eliminating any doubt about the impurities in the natural crocoite. Contact angles were also measured after wiping away the precipitate formed on the surface for concentrations of 500 mg./litre or more of KEtX.

A singular case quoted by Wark and Cox is that of marcasite and pyrites which are of the same chemical composition, FeS_2, but of a different lattice structure. From the point of view of the adsorption theory, a difference in their flotative properties is not unexpected since their minerals might display different valency forces at the outer surfaces of their crystals. It was found that, with a 25 mg./litre

solution of potassium ethyl xanthate and for pH values between 8 and 10 especially, more sodium cyanide was required to prevent contact at marcasite surface than at pyrites. It would be difficult to explain this behaviour by Taggart's theory because the oxidised surfaces for the two minerals would be of the same chemical composition and hence would show the same reactions towards the reagents.

Finally, Wark and Cox questioned the existence of some of the insoluble salts mentioned by Taggart. They considered the compounds, supposed to be produced from p-nitro-benzene-azo-resorcinol and magnesium, nickel and cobalt, as actually lakes, with the dyestuffs adsorbed on magnesium, nickel or cobalt hydroxides. In the reaction between aluminium and α-hydroxy quinoline, the aluminium reacts with the hydroxyl group and not with the nitrogen atom. Then Wark and Cox pointed out that in the complex precipitate, $Cu(en)_2(CdI_4)$, formed from a mixture of potassium iodide and copper ethylene diamine nitrate, it is the copper and not cadmium that is bound to the ethylene diamine group.

From the above review of the two theories, it can be seen that most of the experimental facts are in favour of the adsorption theory. There is no doubt about the compound formation in the case of some metallic sulphides and the xanthates since the metallic xanthates could be leached out and identified. But the reaction theory fails to account for much of the flotation phenomena observed with the non-sulphides.

To give a few more examples, one may consider first the flotation of graphite and sulphur. It is well known

that the flotation of these substances is increased by the addition of xanthates although no xanthate compound of either graphite or sulphur is known to exist.

Then, the separation of sylvite (KCl) from halite (NaCl) suspended in their own saturated brine is an interesting recent development. In one process, sylvite is floated away from the halite by a cationic reagent of the amine type with starch as a conditioning agent and with a frother. In the other process, halite is caused to collect in the froth and the sylvite passes into the underflow using coconut oil or naphthenic acid. One cannot easily imagine compound formation in either of these two flotations.

While the adsorption theory can adequately explain almost all the phenomena observed in flotation, the instances of double decomposition could be regarded as being due to chemisorption or exchange adsorption as suggested by Wark and Cox. According to mineral-bubble contact requirements, an oriented layer of collector molecules or ions is essential and this can only be brought about by some sort of adsorption of the collector on the mineral surface. This consideration alone carries a great weight against the reaction theory.

Recent Theory on Collection.

After nearly twenty years of indecision over the question of the true theory of collectors, a new theory, based on the physical adsorption of heteropolar neutral molecules, was put forward by Cook and Nixon in 1949.(21).

They contended that the 'anionic' and 'cationic'

collectors act simply through the free acids and bases formed in solution by hydrolysis of the corresponding 'anions' and 'cations' respectively. Whether a chemisorption or physical adsorption is to occur is decided by the height of the potential energy barrier to be traversed. The height of the energy barrier determines the activation energy for the chemisorption process. An example given was that of oleic acid in flourite flotation. At room temperature physical adsorption takes place and both flourite and gangue minerals are floated, but on pretreating the ore at 100°C for 5 or 10 mins. in oleic acid solution selective flotation of flourite alone takes place, due supposedly to chemisorption on the flourite.

Criticising the ionic adsorption theory of Wark and Cox, they stated that, if ions were adsorbed, the adsorption would be restricted only to the compact double layer and not to the diffuse layer, in order that the surface may be hydrophobic and the adsorption selective. For the correct orientation, the collector 'ions' would need to be adsorbed with their counter ions in pairs. Assuming that the counter ions were not adsorbed at the same time as the collector ions, they showed by a simple diagrammatic consideration that the energy required for the collector ion to be adsorbed on the crystal lattice with the hydrocarbon chain away from the surface would be of the order of 50,000 calories which was considered to be rather a high value.

Secondly, assuming an unimolecular adsorption on the

mineral particles, the total charge on the counter ions left behind in solution, after having achieved contact between particles and air bubbles, would be also an improbably high figure.

It is suggested that the counter ions would be hydrogen ions and/or the cation of the original collector salt with 'anionic' collectors and hydroxyl ions and/or the anion of the salt with 'cationic' collectors. The direct exchange of collector 'ions' with lattice ions, as proposed by Wark and Cox, is considered to be a remote possibility as, for example, in the case of xanthate ions replacing sulphide ions of the heavy metal sulphide crystals. The main objection to Taggart's theory is the absence of any explanation for the selective deposition of the precipitate on a particular mineral and not on others in spite of its mobility.

One remarkable feature of Cook and Nixons' work is that it clears away some of the anomalies observed in the previously obtained contact bubble data mostly those done by Wark and Cox. The first instance cited was the interpretation of critical pH vs. collector concentration curve for potassium amyl xanthate on sphalerite, on the basis that the effective collector is the free xanthic acid. The formation of the free acid is by hydrolysis as in the equation:-

$$X^- + H_2O = HX + OH^-$$

Thus, if x = the concentration of the free acid HX,

m = the concentration of collector salt added,

and K = the equilibrium constant of the free acid,

$$K = \frac{(H^+)\ (m-x)}{x}$$

$$\text{i.e., } x = \frac{m(H^+)}{(H + K)} \qquad \ldots\ldots\ldots\ldots\ (1)$$

According to the free acid theory of these authors there should be a critical concentration of effective collector (HX) in solution in order to obtain bubble contact; i.e., concentration of HX is constant along critical concentration vs.pH curve. They assumed that m and x are not appreciably altered by adsorption.

Similarly, for cationic collectors, the free base formation is given by,

$$R^+ + H_2O = ROH + H^+$$

$$\text{and } y = \frac{m(OH^-)}{(OH^- + K)} \qquad \ldots\ldots\ldots\ldots\ (2)$$

Using the above equations (1) and (2), they obtained collector salt concentration vs. critical pH curves which agree very closely with the experimental curves of Wark and Cox. The systems examined were potassium amyl xanthate on sphalerite diethyl-, dibutyl-, and di-n-amyl dithiocarbamates on sphalerite and sodium aerofloat on pyrite, galena and chalcopyrite.

Applying their theory to paraffin-chain salt collectors, these authors stated that although chemisorption can account for the action of these collectors on heavy metal sulphides complicated only by instability of the collectors and sometimes by extremely low critical HX values, a further complication arises in the form of physical adsorption. The latter type of adsorption is the predominant factor in the

case of the paraffin-chain salts at ordinary temperatures, and to this was attributed the non-selectivity at low concentrations, and the formation of a double layer with polar-end away from the solid surface in the second layer, at high concentrations. Here too they interpreted with success the contact-bubble curves obtained by Rogers, Sutherland, Wark and Wark (22) and also those obtained by Plante (23).

The critical concentration, x, was supposed to be dependent upon solubility product in some cases, since the solution should be saturated with respect to the chemisorption product for stability. In other cases, the adsorption potential or free energy of the adsorption reaction, may be the determining factor for x. The explanation for the very low critical concentration of xanthic acid on some minerals like galena and chalcopyrite was given on the basis of the high adsorption potential and the very low solubility product.

In so far as the mechanism of collection is concerned, this latest theory is in support of the earlier 'Adsorption Theory' of Wark and his colleagues. Besides satisfactorily explaining the contact-bubble curves obtained by other workers the theory is lacking in direct experimental proof such as that of finding the abstraction by the solid of whole neutral molecules from solutions and not of the effective collector ions only. The arguments advanced were quite sound and based on the already established Electrokinetic Theory and the Theory of Absolute Reaction Rates of Eyring (24). It is possible that the xanthic acid and the long-chain fatty acids are

adsorbed as neutral molecules. Rogers and Sutherland (25) had found from captive-bubble tests that if a reagent can be both ionic and non-ionic and contains a dissociable hydrogen atom, for low pH values below pH_a the anionic (fatty) acids are predominantly non-ionic, and for pH values above pK_a the cationic (amines) acids are predominantly non-ionic. These authors also discovered that free palmitic and lauric acids in acid solutions are the effective collectors in their experimental flotation of galena by the sodium and potassium salts of these acids.

The above summary of the three main theories on collection is designed to show to what stage the knowledge regarding the fundamental principles of flotation has reached. The more important point is that it indicates the line along which future research should be directed in order that the problem may be solved. Investigations on adsorption at gas-solid interfaces have revealed to some extent the nature of solid surfaces. Furthermore, the use of X-ray and radioactive tracers has helped to throw more light on the study of solid surfaces and may eventually lead to the understanding of adsorption at solid-liquid interface. Already research with radioactive tracers has been carried out by Gaudin and his co-workers (26). Such investigations with tagged reagents, designed to attack right at the seat of the phenomenon, namely, the solid-liquid interface, would go far towards explaining the accumulating experimental data in flotation that are at present lacking a sound theoretical basis.

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REAGENTS.

Chapter III.

Purification of Fatty Acids.

Fatty acids are the principal reagents used in the following investigations. They were obtained from B.D.H. and other sources. All the lower acids up to n-caprylic were used as received (B.D.H.) with the exception of one sample of n-propionic and n-caproic acids. These two acids were re-distilled with a Fenske fractionating column, collecting the fractions boiling at 141.3°C and 205°C respectively.

The higher fatty acids, lauric, myristic, palmitic and stearic, were all technical reagents and accordingly further purification was carried out by recrystallising three times from absolute alcohol. This process was resorted to as it was considered that the acids were already purified to a good extent and that purification by esterification and acidification was too tedious and unjustified for the purity required in the present work.

Purity of Acids.

The purity of the lower acids was checked by determining their densities. Where no density data were available the refractive index method or titration method was used. As for the higher acids, from lauric to stearic acid, setting point was used as the criterion of purity. The following table gives the experimental density, refractive

index, titration and setting point values and the corresponding purities:-

TABLE (1)

Formic acid	D_{20} °C	=1.220 .... 100%	(a)
Acetic acid ..... (glacial)	100% by titration with standard NaOH		
n-Propionic acid..	D_{30} °C	=0.7999.... 98.6%	(a)
n-Butyric acid....	D_{25} °C	=0.9567.... 98.5%	(b)
n-Valeric acid....	D^{D}_{20} °C	=1.4110....100%	(c)
n-Caprioc acid....	$n_2{}^{D}_{0}$ °C	=1.4163....100%	(c)
n-Caprylic acid...	$n_2{}^{D}_{0}$ °C	=1.4216....100%	(a)
Lauric acid.....	F.P. = 44.0 °C	... 100%	(d)
Myristic acid.....	F.P. = 53.9 °C		
Palmitic acid.....	F.P. = 62.6 °C		
Stearic acid.....	F.P. = 69.8 °C		

(a) = International Critical Tables, Vol. III. pp.112,122(1928)

(b) = Tables Annuelles de Constantes,Vol. 9,p.29,(1929).

(c) = Handbook of Physics and Chemistry, (1948).

(d) = p.114 of "Fatty Acids", K.S. Markley (Interscience Publishers Inc., N.Y.) 1947.

Sodium Soaps.

Sodium salts of the acids, from valeric to stearic, were prepared by neutralising the acids with caustic soda, both being alcoholic solution. Phenolphthalein was used as external indicator. Concentration of the solution by evaporation predipitated the sodium salt which was recrystallised from alcohol. The crystals were filtered, washed with a

little ether, dried in a vacuum oven and kept in a vacuum desiccator. Their purity was not checked because the acids were taken as pure and the caustic soda used was an analytical reagent.

Inorganic Reagents.

The following substances used in this work were all reagents of A.R. standard as supplied by the manufacturers:- Caustic soda; sulphuric acid; nitric acid; sodium carbonate; sodium sulphate; ferric chloride, sulphate, and nitrate; barium chloride.

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FROTHING PROPERTIES OF THE LOWER ACIDS.

Chapter IV.

It has been stated previously that the polar-non-polar structure confers upon the simple straight-chain fatty acid molecules surface active property which is evident not only in the power to adsorb on mineral surfaces but also at the air-water interface. The latter manifests itself in the frothing property of the lower soluble acids and the soaps of both the lower and higher members. Although the froth stabilities of the lower acids has been studied by Bartsch (27) using the 'static' method of shaking the acid solution in a cylinder and measuring the time to collapse, systematic research into this subject has been lacking as far as the 'dynamic' method resembling more closely the foam formation met with in practice, is concerned. Furthermore, W.Gibb (28), having built up the frothing apparatus described later, has already investigated the frothing properties of the lower alcohols and it was, therefore, thought that it would be interesting to compare the frothing properties of these two homologous series which differ only in respect of the polar group. It was also considered that, as the lower acids possess little or no collecting power for minerals, they might be employed effectively in flotation as frothers if their frothing characteristics were understood properly. For these various reasons, therefore, a study of the frothing power of the lower acids was made.

Theory of Froth Formation.

Before dealing with the experimental work it will

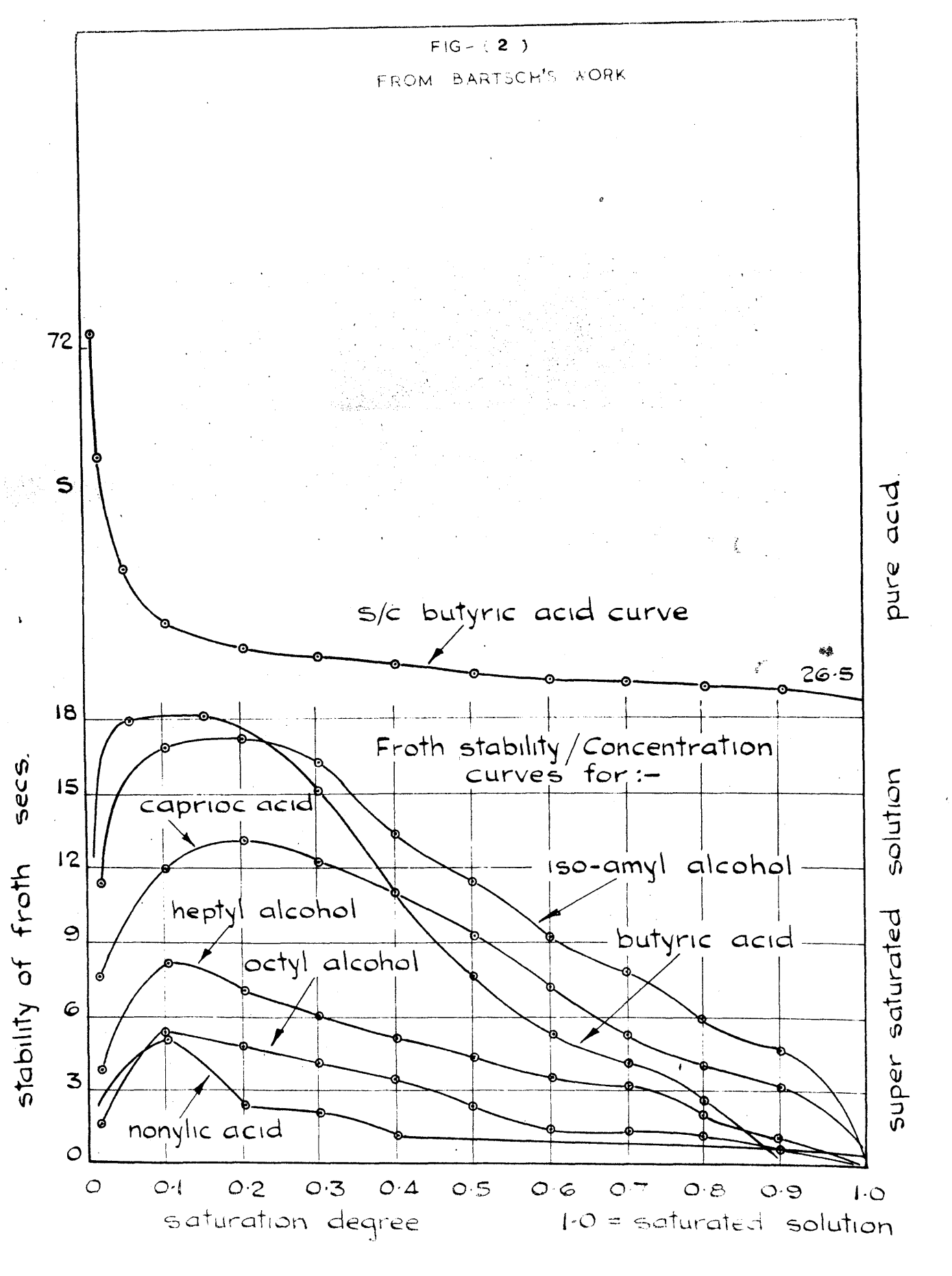
be of advantage to consider the previous work done on the subject and the theories proposed. It was known that pure liquids do not froth and that the frothing power of a solution alters with concentration of solute. Foam can not be produced if the solute is not capillary active, i.e. if it has no influence on the surface tension of the liquid. Since, however, most dissolved substances affect the surface tension of the solvent, most solutions form froth to some extent. Thus aqueous solutions of organic acids and their soaps, sugars, alcohols, etc., which lower the surface tension of water, can be readily induced to foam, as to a lesser extent can aqueous solutions of inorganic salts which raise the surface tension of water. This led to the idea that surface tension is related in some way to the froth formation.

A systematic study on frothing was first carried out by Bartsch (29). He produced froth by shaking a definite volume of the solution in a stoppered bottle and took the time for the bubbles to collapse as a measure of froth stability. He plotted the stabilities in seconds against concentration as shown in Fig. (2). The curves indicate that after a certain concentration the froth stability decreases, having attained a maximum at a low concentration value. The upper curve (s/c) for butyric acid shows that at higher concentrations no obvious relation exists between the surface tension and concentration. From his work, Bartsch arrived at the following conclusions:-

(a) at relatively low concentrations, the maximum frothing

FIG- (2)

FROM BARTSCH'S WORK



power is reached for aqueous solutions of surface active substances such as organic acids and alcohols.

(b) The influence of surface activity on frothing power is limited by the solubility of the solute. Thus in a homologous series of organic compounds the maximum surface activity is attained by the highest members while the maximum solubility is shown by the lowest members. As a result, the intermediate members prove to be best frothers; e.g., amyl alcohol and butyric acid.

(c) The frothing power of a solution depends on the presence of a steep concentration gradient between the surface layer and the body of the solution as is suggested by Gibbs' adsorption equation.

(d) High viscosity of the solution favours froth stability.

(e) The addition of a second substance to the solution affects the frothing power in the same manner as it does the solubility of the surface active substance. For example, nonylic acid, which froths very little in aqueous solution, froths very well in 60 per cent. aqueous ethyl alcohol solution.

Adsorption at Liquid Surfaces.

Bartsch, Hildebrand and Edser (30), all agreed that some surface concentration or adsorption of the frother is necessary for foaming. It was J.W. Gibbs in 1876 (31) who proved thermodynamically that if the addition of a solute lowers the surface tension of the solvent, then the concentration of the solute in the surface layer is greater than that in the bulk of the solution. He derived a fundamental thermodynamical relationship from which the

following approximate equation can be deduced.

$$U = - \frac{c}{RT} \cdot \frac{ds}{dc}$$

where U = excess concentration of the solute at the surface layer,

c = concentration of the solute in the bulk solution,

R = gas constant,

T = absolute temperature,

and

$\frac{ds}{dc}$ = the rate of change of surface tension with concentration.

It is clear, from the above equation, that if $\frac{ds}{dc}$ is negative, the solute is adsorbed, or in excess at the surface. If, however, $\frac{ds}{dc}$ is positive, U will be negative and so the concentration of the solute at the surface will be less than that in the solution. To the first case belong all the organic frothers while to the second belong most of the inorganic salts.

The validity of this equation had been tested by many investigators. Zawidski (31) proved that, with saponin solutions, the concentration in the surface layer is greater than that in the interior of the solution. Lewis (33) determined the excess concentration of various solutes at the interfaces of various solutions and hydrocarbon oils and found that, in nearly all cases, the experimental values for U were much higher than those calculated from Gibbs' equation.

Shorter (34) too observed a similar discrepancy while working with soap, saponin and albumin solutions. He showed this to be due to the fact that the formation of surface layer proceeds for several weeks without reaching an equilibrium unlike a solution of acetic acid where equilibrium is established very rapidly; the separation of the solute from the body of the solution taking place irrespective of the thickness of the layer. Consequently, he interpreted that Gibbs' equation holds only for those instances where the surface layer is thermodynamically reversible. The process of adsorption in the case of soap and saponin solutions was taken as thermodynamically irreversible. He even classified the frothing solutions into three distinct groups having the following characteristics:-

1) ... Surface adsorption thermodynamically reversible with absence of viscosity or rigidity of surface.

2) ... Surface adsorption thermodynamically irreversible with absence of viscosity or rigidity of surface.

3) ... Surface adsorption thermodynamically irreversible with viscous or rigid surface layer.

Again, from the point of view of concentration, Bartsch pointed out that maximum frothing depends upon the sharp drop in concentration of the solute between surface layer and the solution body. This does not apply to skin-forming substances, in which case the surface adsorption is very great and the concentration drop is, therefore, very steep. Thus when the concentration of the solute is very low, the

Gibbs' layer is made up of mostly the water molecules but when the concentration is very high, as it is with saturated solutions, the layer is mainly composed of the solute molecules. At these two extremes the layer is practically homogeneous with respect to one of the two types of molecules. The intermediate concentrations will, therefore, give rise to heterogeneous boundary layer and this heterogeneity is probably the cause of froth formation. This theory explains the low frothing power of the very dilute and the very concentrated solutions.

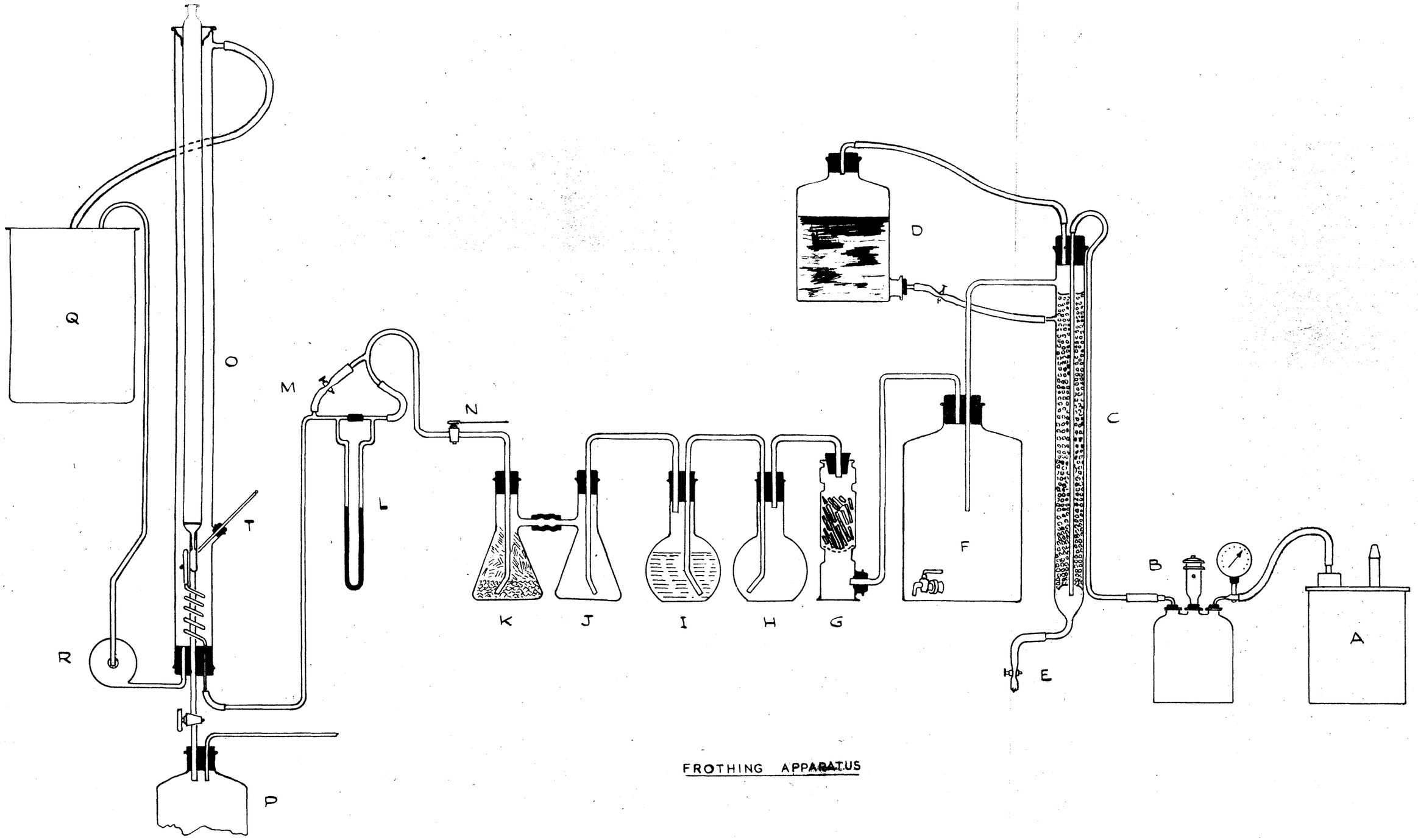
Experimental.

From the foregoing statements, it is obvious that the Gibb's equation can be applied safely to the systems involving relatively small surface-active molecules as those of the lower straight-chain fatty acids, for the theoretical reversible adsorption is approached in such systems. For measurement of froth stabilities, the simplest method is that adopted by Bartsch. Although an average degree of accuracy can be achieved, the method is rather crude and the amount of froth formed depends upon personal vigour, time of shaking, heat from hand reaching the containing vessel etc.

Frothing Apparatus.

The apparatus used in the present research was a modified form of the bubble column or "dynamic foam-meter" introduced by Foulk and Miller (35). The essential part of this apparatus is a long tube with a porous diaphragm at the bottom through which air is passed. With a potential frothing liquid in the tube a froth is produced which rises

FIG - (3)



FROTHING APPARATUS

up until the rate of destruction of bubbles at the top of the mass equals the rate of formation of bubbles at the bottom. At a constant rate of air flow the height reached by the froth above any convenient datum line may be taken as a measure of the frothing stability.

The frothing apparatus is shown in Fig. (3) and the frothing tube is drawn in detail in Fig. (4). The apparatus may be conveniently divided into three sections:-

(i) The air supply, its purification and measurement.

(ii) The frothing tube.

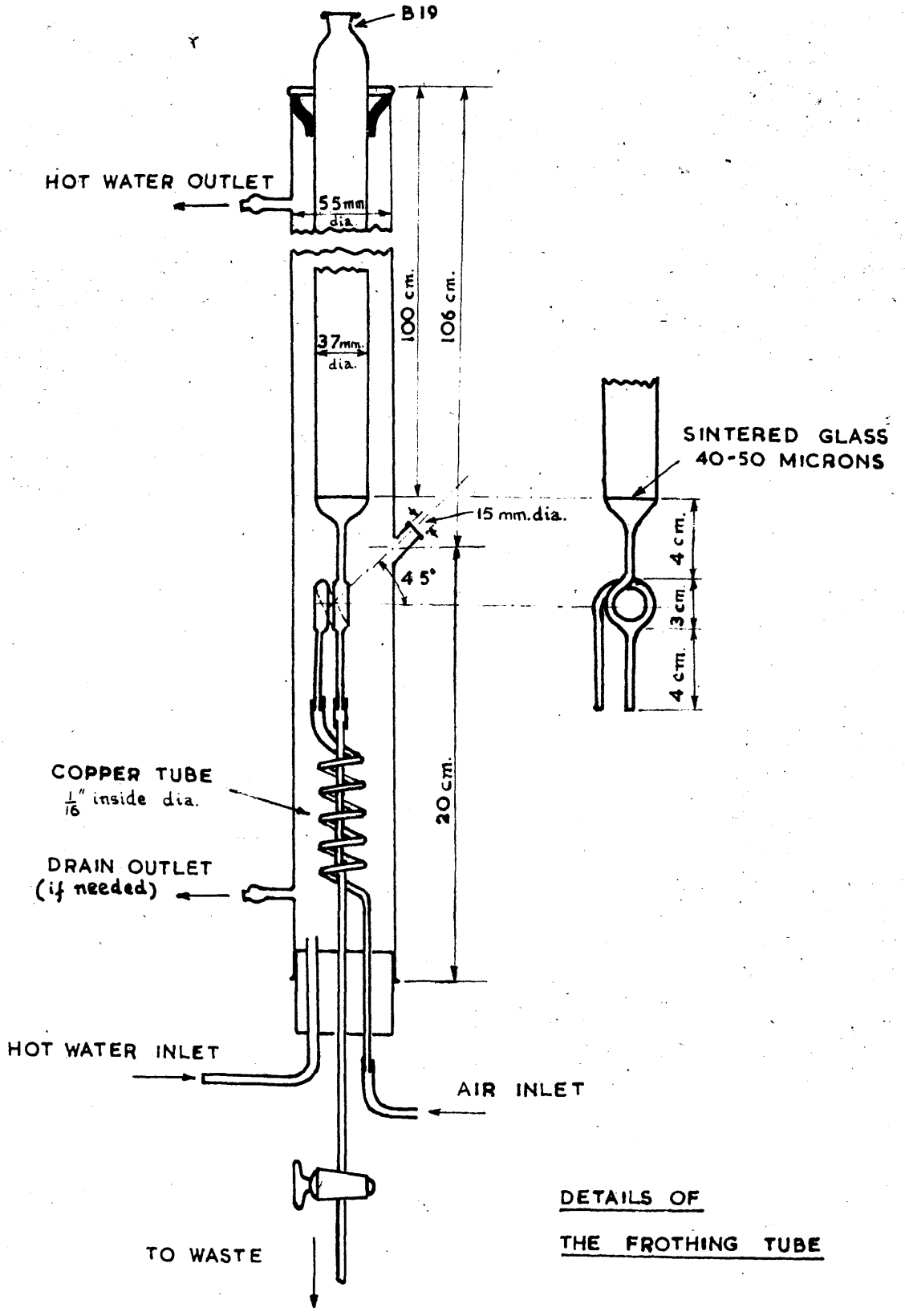
(iii) The thermostatic circuit.

(i) The Air Supply.

The air through the system was supplied by a motor-driven oil vacuum pump A through its exhaust side. The pump was found to operate with more than 10 lb./in^2 back pressure on the exhaust side and as the volume rate of air supplied was more than that normally required, a spring loaded valve fitted to a Woulfe's bottle, B, as shown in the figure, was used to bleed off the excess air. The valve can be adjusted to keep the air at the operating pressure of 8 lb./in.^{2}. The Woulfe's bottle served also to trap both the oil and grease vapours from the pump and the water sucked in from the scrubber, C, on stopping the air-pump. The purification train was necessary to remove oil droplets from the pump and the dust, vapours, etc., from the air to be used in the frothing. Its first member is the scrubber, C, filled with glass beads. This could be filled with water from the reservoir, D, periodically,

as required, and the waste water drained away by opening the clip E. The water carried over by the air from the scrubber was caught in the trap, F, which also acted as an air reservoir, smoothing down the pulsations in the air flow. The water in F was emptied through the cock provided. G to K formed a train of wash bottles for the purification of air. G contained caustic potash sticks to absorb acid vapour and moisture. H was a trap for the saturated solution of chromic acid in concentrated sulphuric acid in the flask, I, which flowed back on shutting off the air supply. J was another trap to catch chromic acid sprays from I. K was filled with silica gel and cotton wool to remove moisture and acid sprays. A glass column, about 2 ft. high, filled with absorbent cotton-wool and silica gel, was not included in the drawing. This was added at a later stage of the experiments to ensure that the air entering the frothing tube was free from all liquid droplets. The air then passed to the flow-meter L. This had previously been found to be more suitable than a pressure gauge for the control of standard conditions due to the fact that the solution in the frothing tube caused the porous disc to have a variable resistance to the air which resulted in corresponding changes of pressure. The flow-meter, L, which was of the orifice type and was calibrated with a wet gas-meter before use, was fitted with a by-pass line closed by a clip M. This by-pass was brought into use when the frothing tube was being cleaned to prevent the high rates of flow then in use from overloading the meter. The main air control cock, N,

FIG-(4)



DETAILS OF

THE FROTHING TUBE

in Fig (5B), was a stop-cock fitted with a notched key and extension handle as was used for delicate control of gas flow-rate in micro-analytical apparatus.

(ii) The Frothing Tube.

The purified air flows into the frothing tube, O, which is shown in more detail in Fig. (4). The tube was of Pyrex glass and was 100 cm. long. The uniform bore of 3.7 cm. narrows down slightly at the base to a sintered glass disc 3.0 cm. in diameter with a porosity of 40-50 microns. The frothing tube was surrounded by a thermostatic jacket. The inlet air is preheated to the same temperature by passing it through a coil of copper tubing placed in the jacket as shown. A loop was made in the air inflow tube below the sintered disc to allow the air to pass into the frothing tube and waste solution to drain away by independent routes. A thermometer, T, indicating the temperature of the water in the jacket, passed through the centre of this loop. The remaining tube from the loop passed through the preheater coil and out of the thermostatic jacket. This tube was fitted with a cock and was connected through a waste solution bottle, P, to the vacuum-line of a water pump. The opening of this stop-cock allowed the tested solutions in the tube to be drained away easily. A paper scale graduated in cm. and mm. was pasted to the back of the frothing tube, the zero of the scale coinciding with the upper surface of the sintered disc. Under the conditions of the experiment a waterproof coating was

FIG - (5)

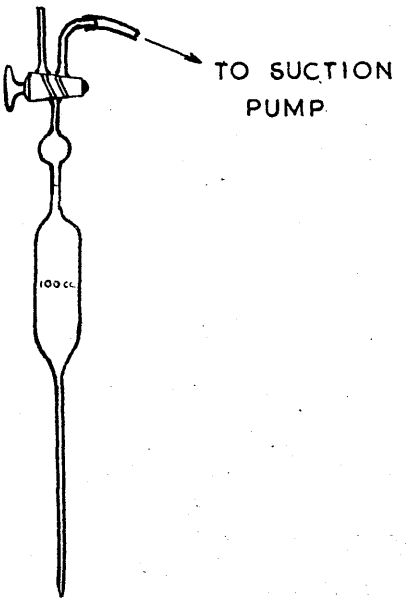


fig-(a)

AUTOMATIC PIPETTE

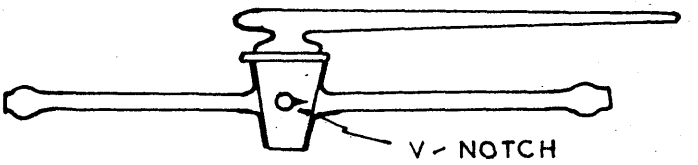


fig-(b)

STOP-CORK FOR
ADJUSTING AIR-FLOW RATE

required to keep the paper scale on the outside of the tube, and thus protect it from the running water in the jacket. The most suitable coating was found to be black waterproof enamel covered with two thin coats of thin shellac varnish. Even this coating had to be renewed after about four weeks of constant use.

(iii) The Thermostatic Circuit.

The jacket water was supplied fron an electrically heated thermostatic bath, Q, circulation being achieved by a small centrifugal pump driven by an electrical motor, R. A special automatic pipette was devised for use in transferring solutions from the stock-bottle to the frothing tube. It is shown in Fig. (5a). In one position of the two-way cock the pipette was connected to the vacuum of the water pump and in the other to the atmosphere. Thus the pipette could be filled without using the mouth and contamination of the solution under test was avoided. In all the tests, water was circulated through the thermostatic jacket to keep the solutions at 25± 0.2°C. A dust cap made from a small beaker, inverted, and filled with cotton-wool, was used on top of the frothing tube during tests.

Preparation of Solutions.

The preparation of the acid solutions was on a weight to weight percentage basis. The volume of acid necessary for making up to the desired concentration was calculated from a knowledge of the density of that particular concentration given in the International Critical Tables. In the case of n-caproic acid, no such data on the variation in density

with concentration was available but as its solubility in water is very low the densities of its solutions were taken as the same as that of water. The double distilled water, condensed on Pyrex glass, was used throughout the experiments.

Frothing Tests.

Absolute care was taken to clean all the bottles and apparatus, especially the frothing tube, with chromic-sulphuric acid mixture. After washing away the chromic acid from the frothing tube with double distilled water, a small volume of the solution to be tested was added to the tube and was frothed for some time. This liquid was next drained away and the tube was then ready for experiment. The dust cap, filled with cotton-wool was always placed on top of the column while the solutions were drawn to waste through the porous disc. A small rate of air-flow was allowed to pass through the tube during the process of evacuation so that no liquid could enter the air-line by means of the loop.

The vacuum line was then closed and keeping the air flow at a very low value to prevent any liquid from permeating through the porous disc, 100 cc. of the solution to be tested were transferred to the tube. The air velocity was brought to the highest value required, as recorded on the flow-meter. A constant air flow rate was maintained by controlling the stop-cock, N, while the temperature of the solution was allowed to reach that of the bath. After five minutes, the height of the froth was read from the scale at the back of the tube.

When the froth level fluctuates, as often happens with solutions having low froth stability, the mean of the upper and the lower readings was taken.

As a check on local contamination of the tube each solution was frothed at three rates of air-flow giving flow-meter readings as in Table (2) below.

TABLE (2).

	Flow-meter Reading (cm.water)	Rate of Flow at Sintered Disc (25°C)
Rate I	2.0	1.44 ft^3 per hour
Rate II	4.0	2.12 " " "
Rate III	6.0	2.71 " " "

Before changing over to the next rate of air flow, the foam was broken up by cutting off the air supply for a few seconds. A new foam was then built up by taking the air flow up to the desired rate. The need for a rigid control of the air flow was discovered when it was observed that even a variation of 2 mm. in the flow-meter reading could cause a change of about 1 to 2 cm. in the froth height. As a check on the readings taken, it was usual to repeat the whole operation by starting with the lowest rate of air flow and ending up at the highest.

The concentration intervals at which the solutions were tested depended on the solubility of the material under

test. They varied from 1 per cent. in the case of the first four more easily soluble acids to 0.01 per cent. for n-caproic acid. The lowest possible concentrations were always chosen to start with so as to obtain a rough idea of the concentration intervals to be employed.

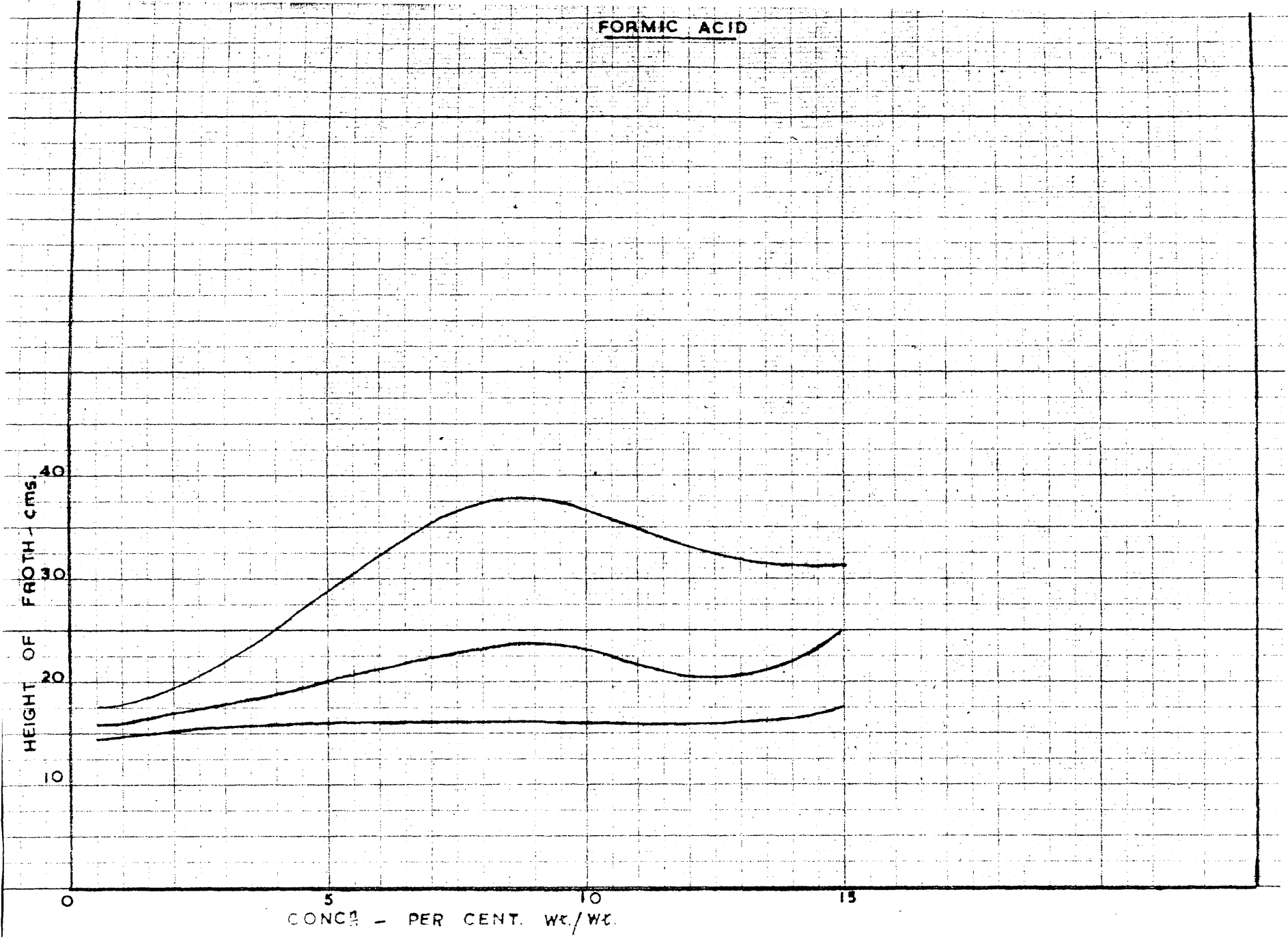
The very low frothing power of formic and acetic acids gave rise to some difficulty in reproducing the results. The readings became more and more irreproducible as the rate of air flow was increased, as is evident from the following table:-

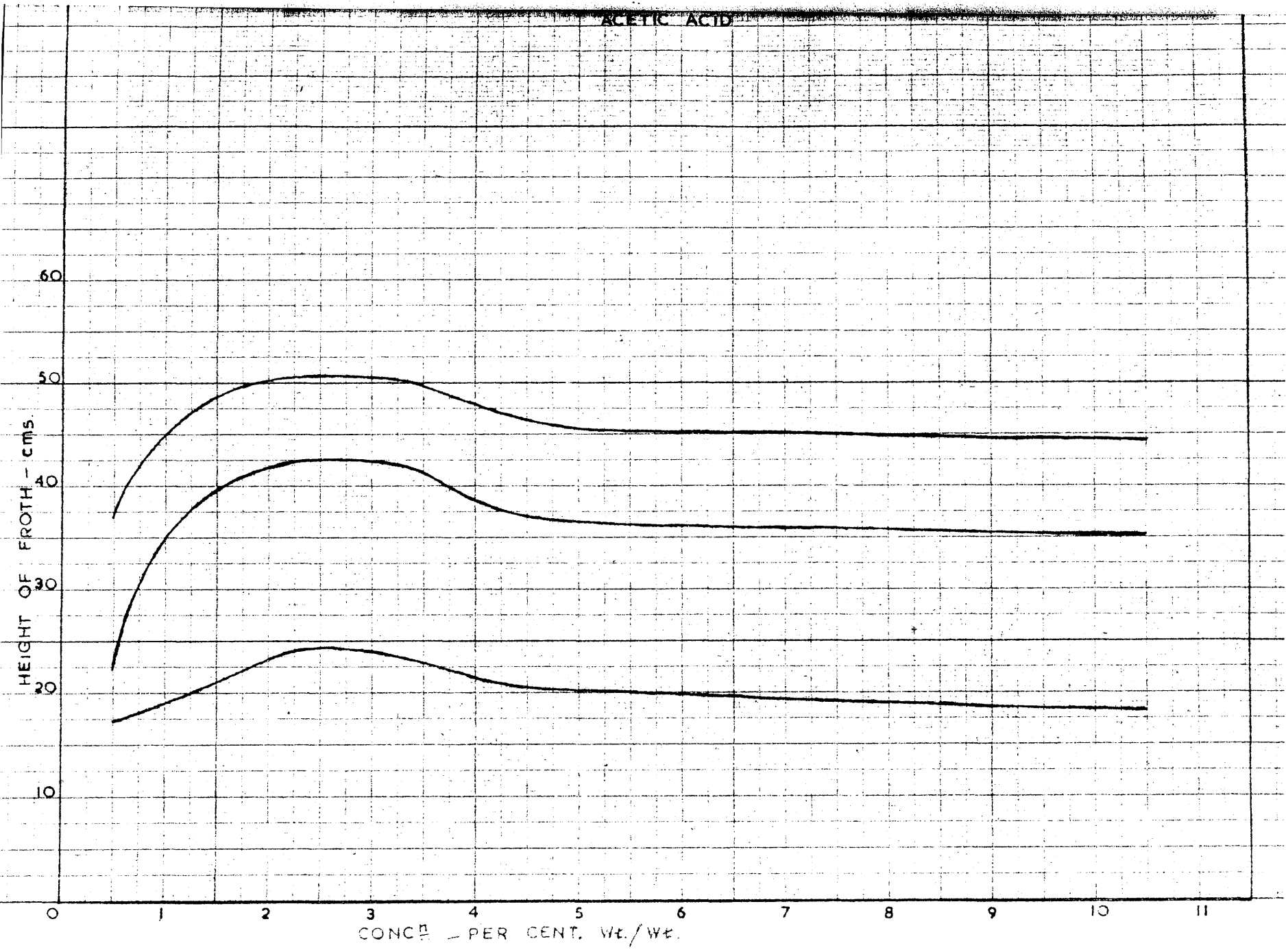
TABLE (3)

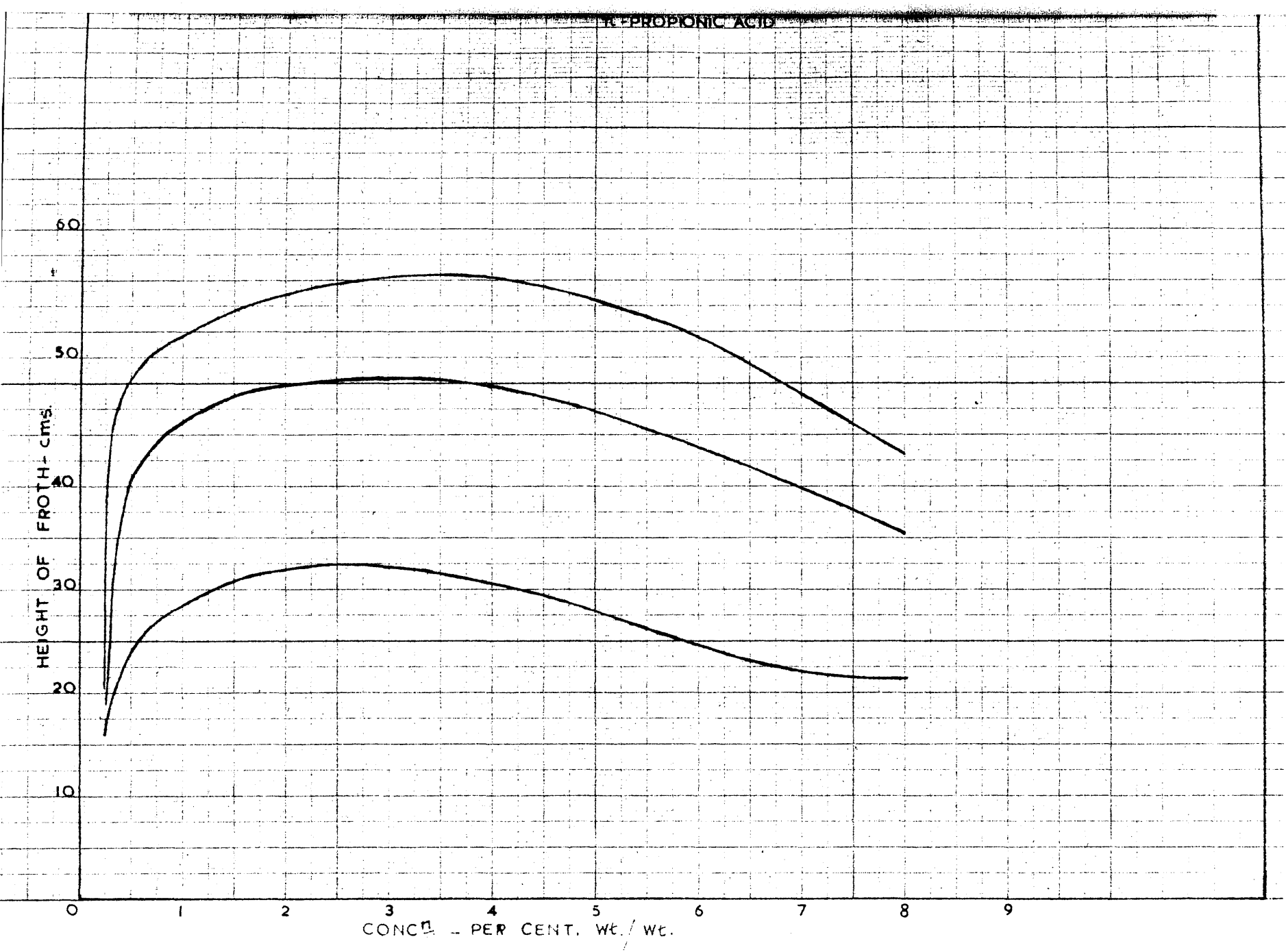
Acid Used	Concn. In wt./wt.%	Froth Height in cms. (1)	(2)	(3)
Formic	9%	37.5	24.0	16.1
		35.0	20.4	16.1
		29.8	20.6	16.5
	8%	38.0	24.0	16.0
		30.7	20.0	16.0
Acetic	2.5%	51.2	41.5	24.5
		50.0	38.5	24.5

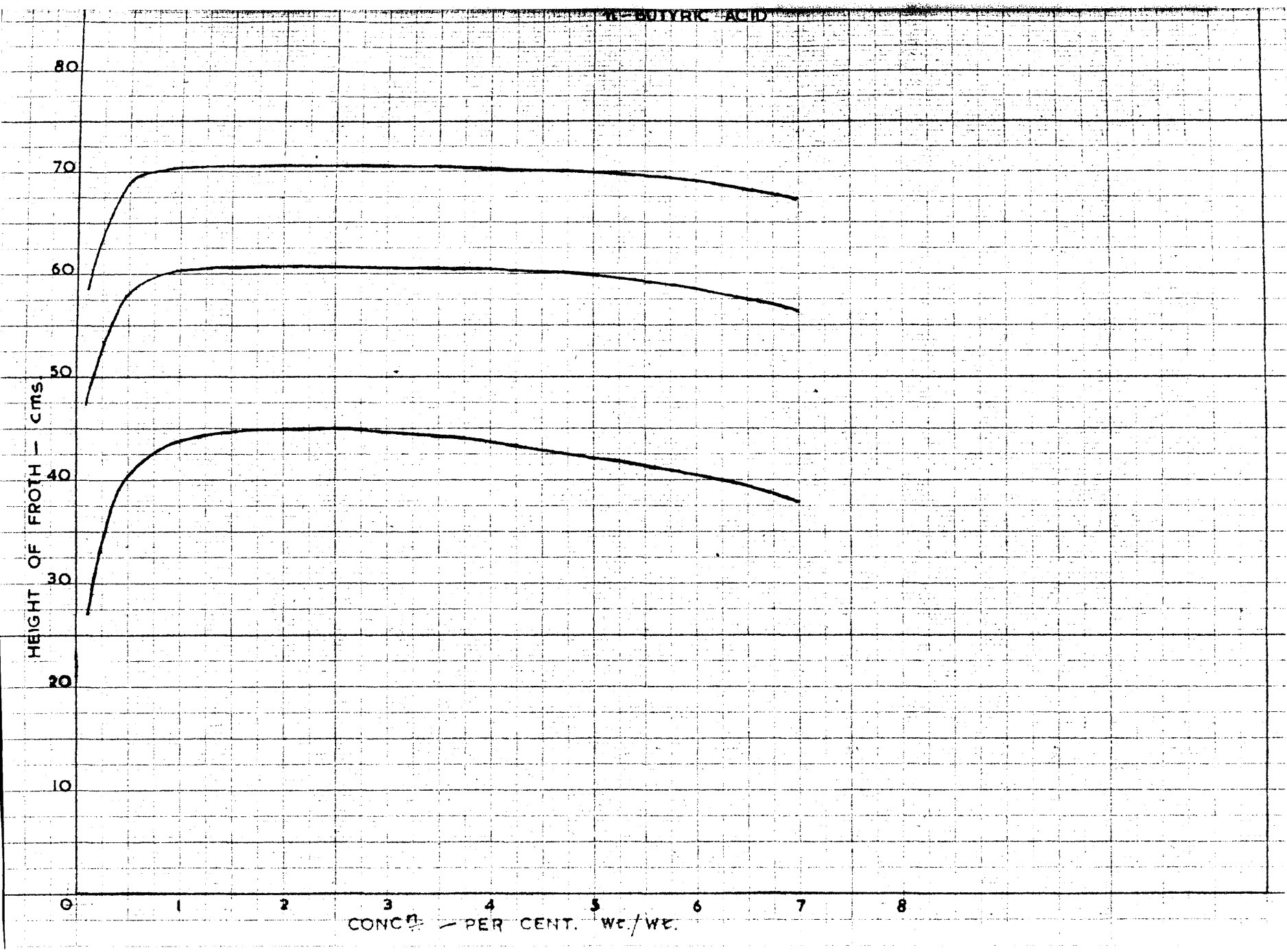
(1), (2) and (3) are air flow rates at 2.71, 2.12 and 1.44 ft^3/hr. respectively.

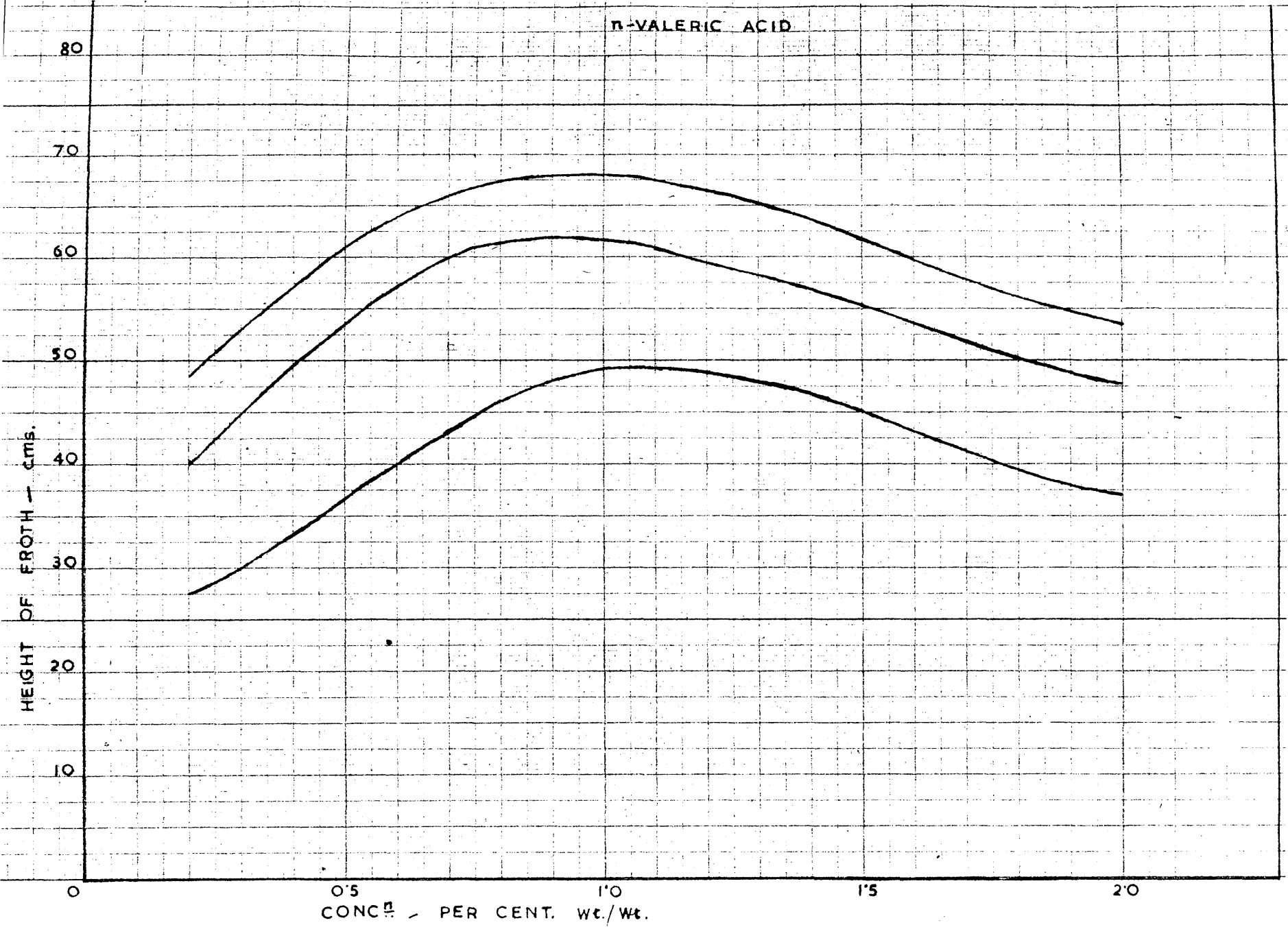
The probable reason for this behaviour is that at a certain rate of air flow the whole of the liquid is turned into froth and the equilibrium is reached between the rates of formation and destruction of froth. Above that rate the excess air ascends the froth column as large bubbles thus

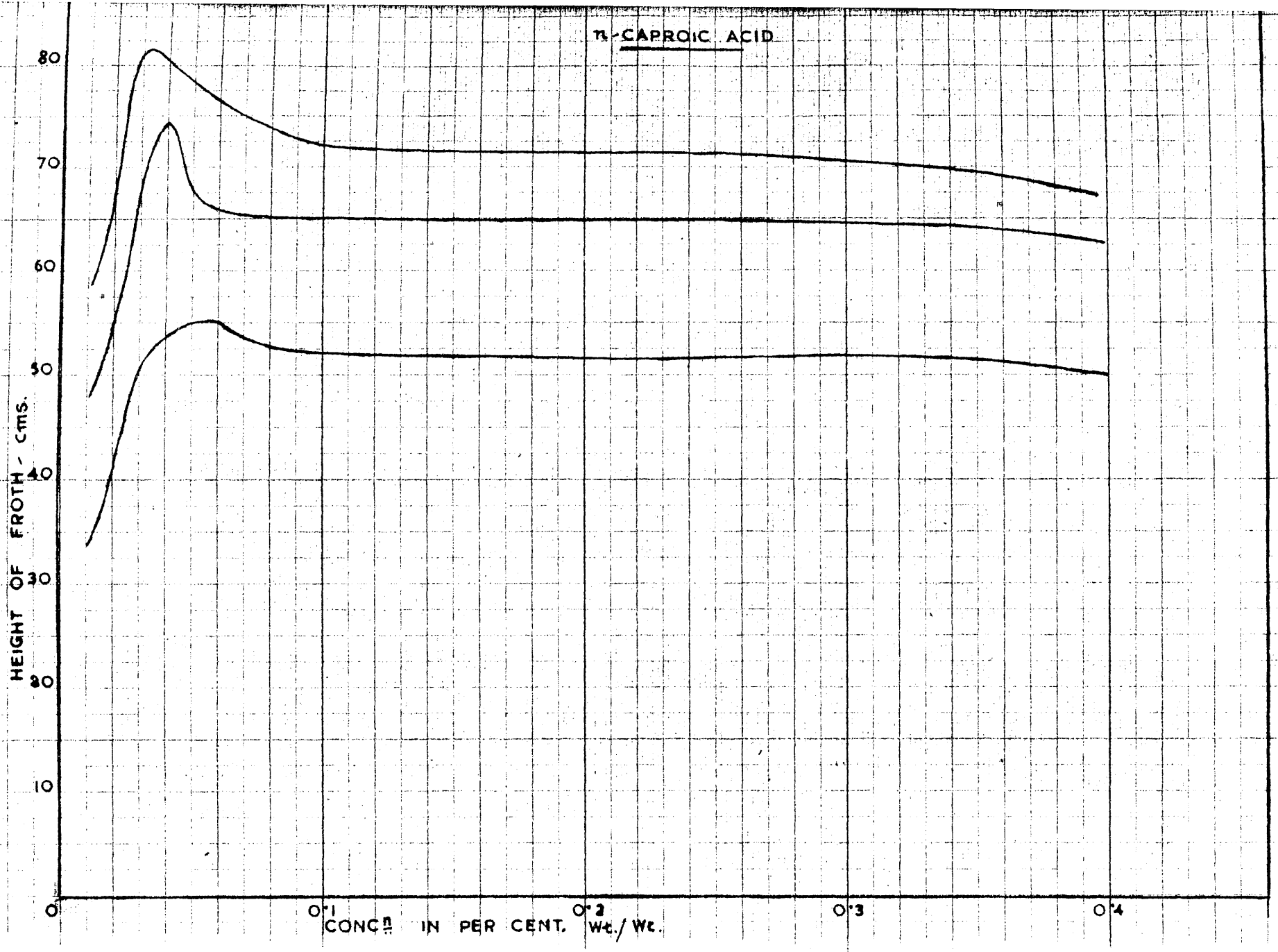

FORMIC ACID
HEIGHT OF FROTH - cms.
40
30
20
10
0
5
10
15
CONCn - PER CENT. Wt./Wt.

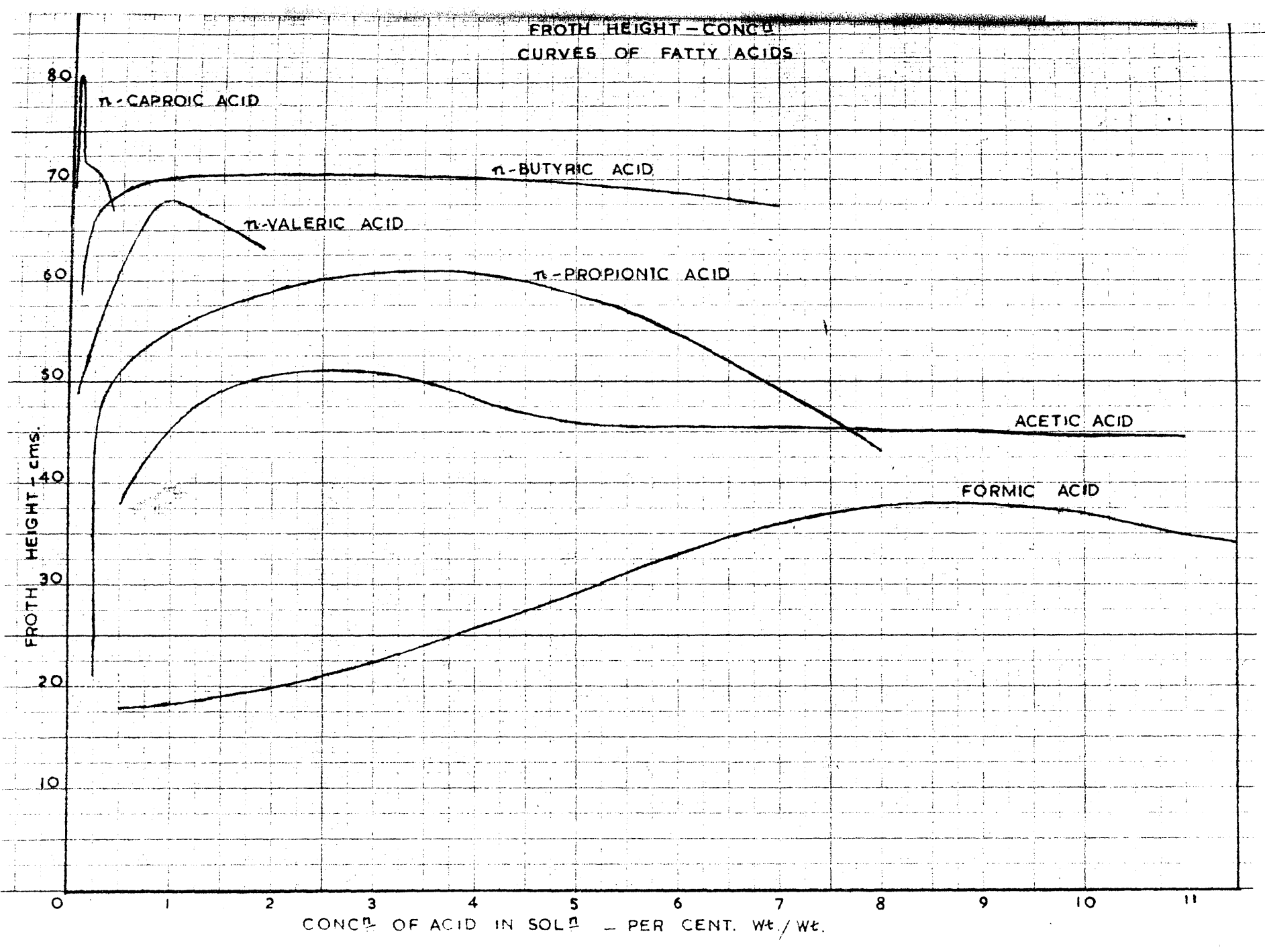

ACETIC ACID
60
50
40
30
20
10
HEIGHT OF FROTH - cms.
0
1
2
3
4
5
6
7
8
9
10
11
CONCn - PER CENT. Wt./Wt.


n-PROPIONIC ACID
HEIGHT OF FROTH - cms.
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
CONCN - PER CENT. Wt./Wt.


n-BUTYRIC ACID
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
HEIGHT OF FROTH — cms.
CONCⁿ — PER CENT. wt./wt.


n-VALERIC ACID
80
70
60
50
40
30
20
10
0
0·5
1·0
1·5
2·0
HEIGHT OF FROTH — cms.
CONCn — PER CENT. Wt./Wt.


n-CAPROIC ACID
80
70
60
50
40
30
20
10
0
HEIGHT OF FROTH - cms.
0·1
0·2
0·3
0·4
CONCⁿ IN PER CENT. Wt./Wt.


FROTH HEIGHT – CONCⁿ
CURVES OF FATTY ACIDS
n-CAPROIC ACID
n-BUTYRIC ACID
n-VALERIC ACID
n-PROPIONIC ACID
ACETIC ACID
FORMIC ACID
FROTH HEIGHT – cms.
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
11
CONCⁿ OF ACID IN SOLⁿ – PER CENT. Wt / Wt.

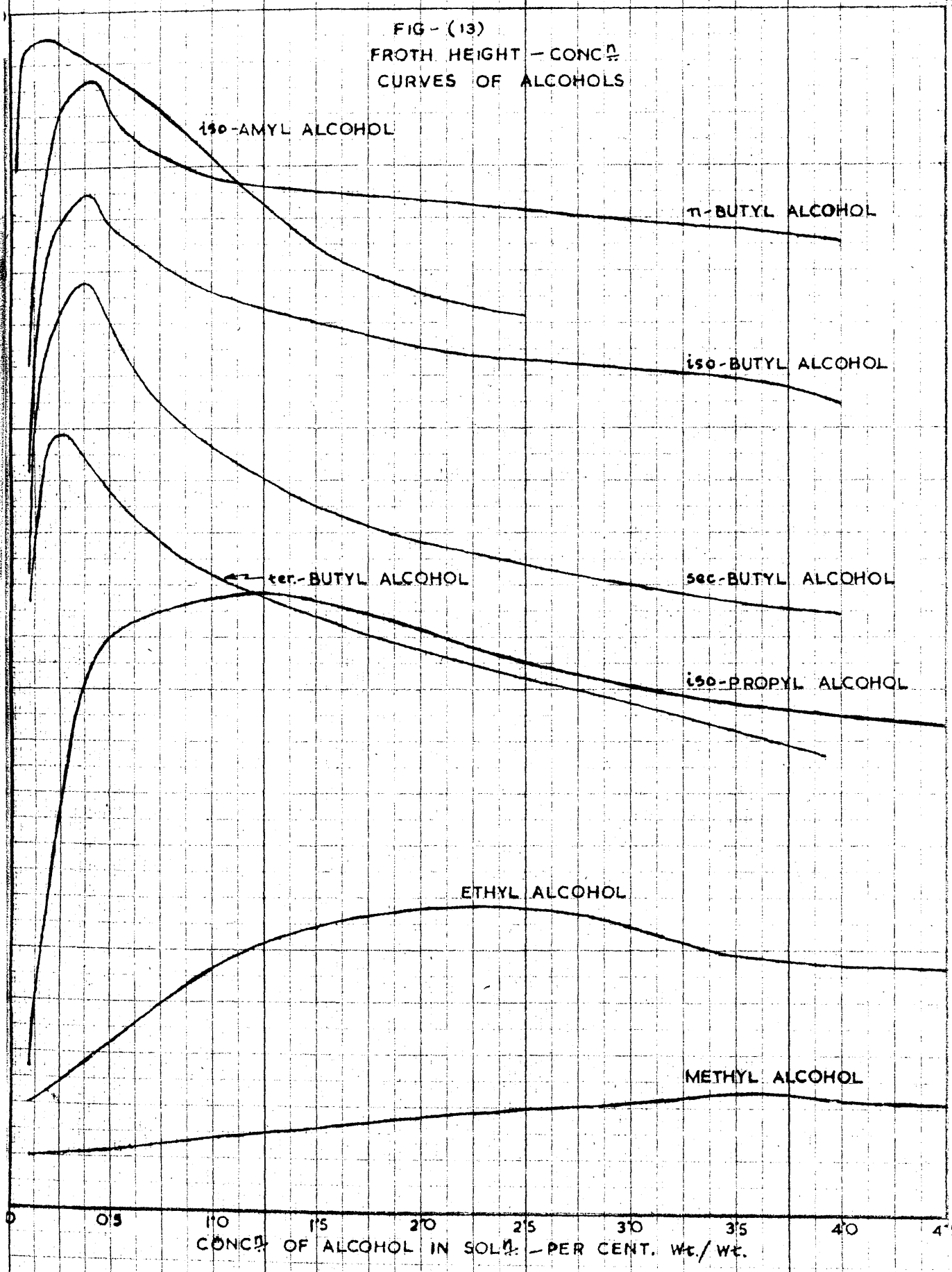


FIG - (13)
FROTH HEIGHT - CONCⁿ.
CURVES OF ALCOHOLS
iso-AMYL ALCOHOL
n-BUTYL ALCOHOL
iso-BUTYL ALCOHOL
ter.-BUTYL ALCOHOL
sec-BUTYL ALCOHOL
iso-PROPYL ALCOHOL
ETHYL ALCOHOL
METHYL ALCOHOL
0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
CONCⁿ. OF ALCOHOL IN SOLⁿ. - PER CENT. Wt./Wt.

disturbing the equilibrium and the froth height may depend on the size and number of these large air bubbles. This difficulty was overcome by repeating the tests a number of times and taking the final mean value.

Results.

The results obtained are set down in figures (6) to (11). The variation in froth height in cms. at each rate of air flow is plotted against concentration. The graphs indicate clearly that the froth stabilities of the acids increase rapidly with concentration to fall again after reaching a maximum at a definite concentration. It may, however, be noted that if it were not for the somewhat pronounced curvature of the lowest curve for n-butyric acid, it would have been very difficult to arrive at the true position of the maximum because of the unusual flatness in the curves for this acid.

The froth height-concentration curves for the highest rate of air flow were put together in one graph as in Fig.(12) in order to compare the froth stabilities of the six acids. A similar comparison of the froth stabilities of the lower alcohols from the results of Gibb is shown in Fig. (13).

An attempt to work with n-caprylic acid, which has a very low solubility of 0.25 gm. per 100 cc. of water at 25°C, did not meet with success owing to the fact that the amount of acid in solution is insufficient to produce a stable froth. Better results with higher acids may be expected if a frothing tube having a smaller bore is chosen and if the working

temperature is raised to about 60 to 70°C.

Discussion of Results.

From figs.(6) to (13), it was concluded (36) that:-

(1) In the concentration range investigated there is a well-defined maximum value of froth stability occurring at a relatively low concentration of the acid, the highest being 8.5% for formic acid. This maximum becomes less sharp as the series is ascended only to become very pronounced after the fourth member.

(2) As the homologous series is ascended, i.e., as the length of the non-polar chain becomes longer, the froth stability of the solution increases. The exception to this rule is n-valeric acid, frothing power of which falls below its next lower member butyric acid. The reason for this is not known. As the higher homologues have not been tested, it is not possible to check up Bartsch's finding that the froth stability decreased after C_5 - C_6.

(3) With increase in molecular weight, i.e., with increase in size of the non-polar group of the acid molecule, the concentration at which the maximum froth stability occurs decreases. The case of acetic acid is anomalous since its maximum is at a much lower concentration than is expected. Its ability to associate into di-acetic acid molecules, with the resultant decrease in the quantity required to saturate the surface of the bubble film, might be responsible for this phenomenon. The estimated molar concentrations for maximum froth stability both for the acids and alcohols are given in Table (4).

(4) From a comparison of the alcohols and their corresponding acids, it is clear that the acids have a greater maximum froth stability than the alcohols and, in general, it requires a higher concentration to reach maximum froth stability for the acids than for the alcohols. Up to the third member in the two series, the frothing power of the acid is about twice that of the alcohol.

(5) The surface tension corresponding to the concentration of surface active substance for maximum froth stability (as obtained from International Critical Tables) is approximately constant thus agreeing with Bartsch's conclusions. The values are given Table (4).

Concentration in the Surface Film.

It had been stated earlier in the theory of froth formation that the frothing property of a solution is related to the concentration of surface active agent and the surface tension. The concentration of the surface active agent in solution at maximum froth stability is of less importance than the actual bulk concentration. The connection between the last two quantities is given by Gibbs' equation. Similarly, the static surface tension value at maximum froth stability is less directly connected with the froth stability than the change in free energy of the surface from the dynamic surface tension of the surface at zero time before adsorption starts to the static surface tension when adsorption is complete. Although there is a decrease in surface tension in the case of solutions under discussion, the solutions are so dilute that their dynamic surface tension approaches that of pure water.

TABLE (4)

Frothing of Solutions at 25°C.

	Maximum Froth Weight in Apparatus (cm.)	Concentration for Maximum Froth Stability.			Approx. Surface Tension at Max. Stability (dynes/cm.)	ds/dc dynes per cm./ moles per litre	UN (Moles/ cm^2.)	$1/UN$ (A^2 per mole)
		W/W per cwt.	Moles per litre	Moles per cent.				
(37)Formic Acid	38.0	8.75	1.90	3.62	64	-2.74	1.27×10^{-14}	78.8
(37)Methanol	18.6	3.50	1.09	2.00	64	-5.68	1.50×10^{-14}	66.7
(39)Acetic Acid	51.0	2.50	0.417	0.747	65	-12.5	1.27×10^{-14}	78.8
(38)Ethenol	25.8	2.50	0.544	0.990	61	-14.3	1.88×10^{-14}	53.2
(41)Propionic Acid	61.0	3.50	0.473	0.848	54	-18.1	2.24×10^{-14}	44.7
(38,40)Iso-propanol	37.8	1.50	0.250	0.460	60	-33.0	2.01×10^{-14}	49.8
n-Butyric Acid	70.5	2.50	0.284	0.510	47	-38.3	2.64×10^{-14}	37.9
n-Butanol	57.4	0.400	0.054	0.098	62	-	-	-
(41)Iso-Butanol	53.2	0.375	0.051	0.092	62	-112	1.38×10^{-14}	72.4
Sec.-Butanol	49.6	0.350	0.047	0.081	-	-	-	-
Tert.-Butanol	43.8	0.250	0.034	0.061	-	-	-	-
(38)Valeric Acid	67.5	1.00	0.098	0.176	40	-119	2.84×10^{-14}	35.2
(37)Iso-Amyl Alcohol	60.0	0.200	0.023	0.041	57	-398	2.20×10^{-14}	45.4
(40)Caproic Acid	82.0	0.035	0.0030	0.0054	66	-1680	1.23×10^{-14}	81.3

Moreover, since the surface tensions of the acid solutions at maximum froth stability are almost equal it seems that their latent ability to form froth is also approximately constant. As no insoluble films are involved the Gibbs' equation should hold more or less accurately for the dilute solutions employed.

The calculation of the excess frothing agent in the surface film was done by first drawing the surface tension-concentration curves from figures given in the International Critical Tables (pp. 467-469. Vol IV. (1928)). In some cases these were not available at 25°C but since the value of $\frac{ds}{dc}$ does not change much with temperature and since it has already been found by Gibb (28) that the position of maximum stability is little affected by change in temperature, values for 30°C or 20°C were substituted where these only were available. The value of the tangent $\frac{ds}{dc}$ to the curve at the required concentration was computed and the required quantity calculated as shown below in the specimen calculation.

Specimen Calculation.

Gibbs' Equation is $U = \frac{-C}{RT} \cdot \frac{ds}{dc}$

where U is the excess concentration of surface active agent per cm^2. of surface,

and C is the concentration of solute in the bulk of the solution.

Thus if N = Avogadro's number = 6.023×10^{23},

$$UN = -\frac{N}{RT} . C . \frac{ds}{dc} \quad \text{molecules/cm.}^2$$

Substituting k for $\frac{N}{RT}$,

$$UN = - k.C.\frac{ds}{dc}$$

Since $R = 8.316 \times 10^{7}$ ergs per degree,

and $T = 298°$ Absolute,

$k = 2.431 \times 10^{13}$.

For acetic acid at maximum froth stability,

C = 2.5 per cent W/W or 0.417 moles/litre,

and from the surface tension -concentration curve plotted from the I.C.T. figures, at 0.417 moles/litre, $\frac{ds}{dc} = -12.5$.

Thus $UN = - 2.431 \times 10^{13} \times 0.417 \times (-12.5)$

$= 1.27 \times 10^{17}$ molecules per $cm.^{2}$

The values of UN for other compounds are given in the Table together with references from which the I.C.T. took the surface tension-concentration values.

In the evaluation of UN a number of errors are possible as, for example, in the original surface tension determinations, in drawing a smooth curve through the points, in the graphical determination of the tangent to the curve at the required concentration value, and in the original determination of this concentration for maximum froth stability. Considering these, it may be said that the UN values obtained are remarkably constant. The reciprocal of UN gives a value for the effective area of surface per molecule of surface active agent. From the Table (4) it could be seen that whereas formic, acetic and caproic acids have about 80 $Å^{2}$ of effective area per molecule, the reamining three acids have about 40 $Å^{2}$ of surface. Thus the occupation of similar

cross-sectional areas in the adsorbed position by such unlike molecules as acetic and caproic acids suggests that they are oriented according to the Langmuir-Harkins' theory; that is, they are standing in the surface with the non-polar group in the gas phase and the polar group in the aqueous phase. The results of Table (4) are thus an indirect proof that the orientation theory holds for these comparatively small and completely soluble molecules as it does for the larger molecules.

The second conclusion that could be drawn from the results is that the maximum froth stability corresponds to a definite concentration in the surface film, independent of the size of the non-polar end of the molecule but in some way connected with the cross-sectional area of the surface active molecule. The calculated area per molecule, in Table (4) last column, for any of the acids is higher than the known values of 16 $\mathring{A}^2$ and 20.5 $\mathring{A}^2$ as found by X-ray methods and by compression of insoluble fatty acid films, respectively. Similarly 21.6 $\mathring{A}^2$ for the cross-section of an alcohol is smaller than the calculated values in the Table. Hence at maximum froth stability the surface film is not saturated with the surface active molecules for each molecule seems to occupy about two to three times its cross-sectional area. Thus the most stable film must be made up of fatty acid molecules and water molecules in a definite ratio and this leads to the conclusion that a stable membrane must have some preferred arrangement of molecules.

Use as Frothing Agents.

Whether a compound is fit to be used as a frothing agent can be judged by a consideration of four important factors; frothing power, collecting power, solubility, and coat. Flotation tests, described later, show that the collecting power of lower acids up to the sixth member is relatively low giving as a maximum 20 per cent. recovery, with barytes. From the point of view of froth stability, n-caproic acid is obviously the best suited for use as a frothing agent. Its frothing power may be compared to that of the isoamyl alcohol. Figs.(11) and (13) show that while isoamyl alcohol gives 59 cms. of froth height at about 0.2 per cent. (wt./wt.) concentration, n-caproic acid gives 81.5 cms froth height at 0.034 per cent. (wt./wt.) concentration. The latter, therefore, seems to possess a greater froth stability than the alcohol. Since amyl alcohol forms the principle constituents of fusel oil used to some extent as a frother in flotation, there is no reason why n-caproic acid should not be used as a frother too. In presence of other collectors its own small collector power should have very little effect. The only disadvantage is its foul smell, but it is not any worse than that of some accepted flotation agents, e.g., xanthates.

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A STANDARDISED FLOTATION TEST

Chapter V.

Laboratory Flotation Cells.

It would not be far from the truth if it were said that at present the flotation test is the beginning and the end of flotation research. One may easily standardise reagents, apparatus, and procedure, but the fact that an ore is an inherently variable and heterogeneous material, and that any two mineral deposits are rarely identical, makes it almost impossible to predict results with any new ore body. An actual flotation test on a small scale is the only answer to the problem.

Taggart (42) gives perhaps the best survey of laboratory flotation cells. A laboratory test may be carried out on any weight of ore between 0.5 gm. and 1 kilogram, and therefore the cell to be used depends entirely on the nature of the minerals being separated, and the weight of material being treated. In most cases the size of the cell to be used depends on the available stock of ore on which the tests have to be carried out.

While there exists a large variety of cells for laboratory purposes, no real effort has been made to relate the dimensions, shape and other factors pertaining to the cell with the flotation results and it is usually taken for granted that the flotation of a mineral with one cell will be reproducible with another. In practice, this is not quite the case.

Flotation tests may be carried out with graduated

shaking cylinders and separating funnels. Only tests of qualitative nature are possible with shaking cylinders, the extent of flotation being given by the height of mineral laden froth on top after shaking. A cylinderical separating funnel provided with a wide mouth and a wide hole was used by Kraeber and Boppel (43). The agitation of the pulp to form a froth was done by means of a small steel piston and the tailings were separated from the floated powder by opening the stop-cock. A similar separating funnel of 100 cc. capacity was used by Wolkowa, Serb-Serbina and Saporosky (44). They added 50 cc. of solution and 10 gms. of powder into the funnel and shaking was done by hand.

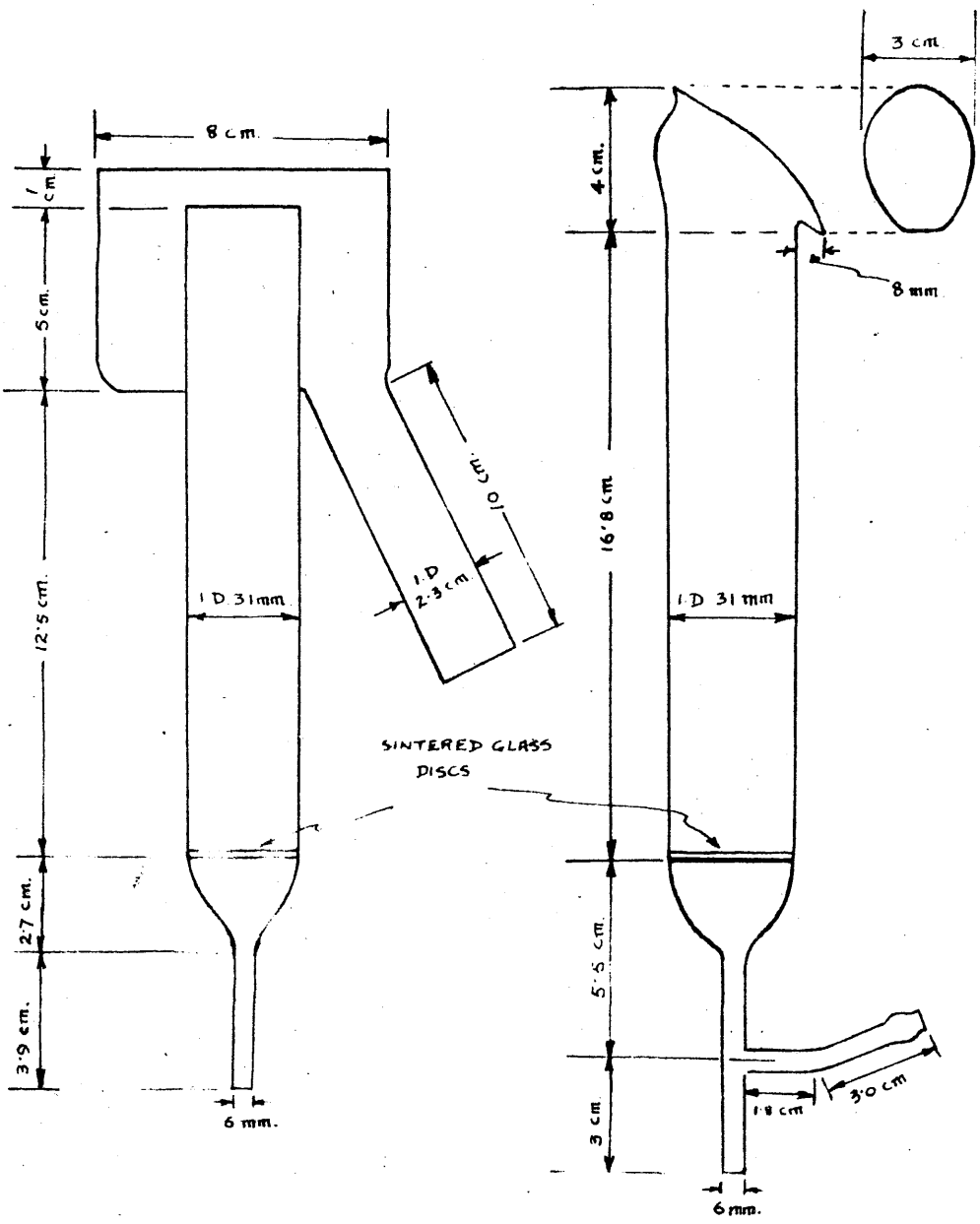
For an ore feed of from 100 to 1000 gms. the author has found the Fagergren Sub-Aeration Cell, manufactured by American Cyanamid Co., very useful. It is simple to operate and gives very reproducible results. For testing quantities of about 50 gms. the University of Utah cell is recommended (45). The Prior Cell (46) is meant for smaller scale laboratory testing and seems to be suitable for rough preliminary work or routine testing. It should be particularly suitable in a laboratory where there is no glass blower available. The Knoll and Leaf Cell (47) and its modifications as applied in this work is particularly applicable to small scale flotation research. It operates on 5 to 20 gms. ore. Finally there is the Hallimond tube which requires only about 0.5 to 1.0 gms. of ore and functions without the use of a frother.

Flotation Cell (A)

In the present investigations the author has

FIG-(14)

FLOTATION CELLS



CELL(A)

CELL(B)

SCALE HALF SIZE

employed three cells all made of glass. The diagram of the first cell with its dimensions is given in Fig. (14). Its design is due to Knoll and Leaf (47) and is described in Taggart's Handbook of Ore-dressing (42). Owing to the difficulties in glass-blowing the shape is somewhat different from the original which had a dome-shaped bottom in the outer receiver instead of the flat one shown in the diagram. The cylinderical tube has a capacity of about 120 cc. and the cell is meant to be used with 5 to 20 mgs. of ore. Knoll and Leaf passed 4 to 10 litres of clean air per minute through the No. 3 sintered glass diaphragm having a porosity of 20 to 30 microns while the overflow was maintained by the addition of the solution at a rate of 2-2.5 cc. per minute.

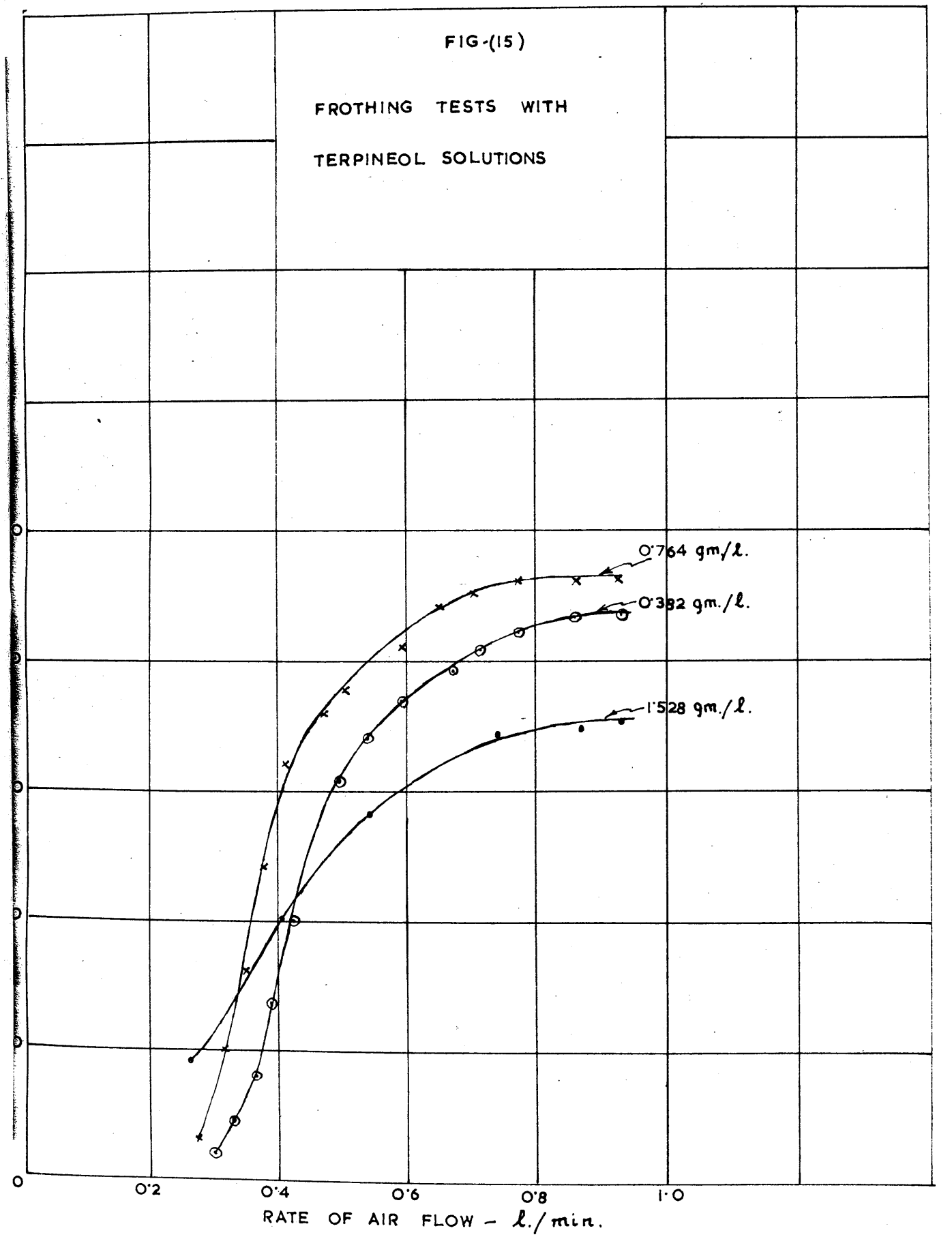
Using a Baird and Tatlock (K.801.H2) sintered glass diaphragm, having a porosity of 40-90 microns, the author found that the above air flow was much higher than was actually needed. 0.75 litre per minute was sufficient for a test. This ideal air flow rate was determined as follows and was used in all later tests.

A frothing test was conducted with three different concentrations of terpineol solutions using the flotation cell as a frothing tube. 75 cc. of the solution to be tested was added to the cell while a small current of air was maintained to prevent any liquid from passing through the sintered disc. The air flow rate was raised gradually until the froth produced started to overflow into the outer cup. Keeping the air flow constant at that initial rate the volume of the total overflow

FIG-(15)

FROTHING TESTS WITH

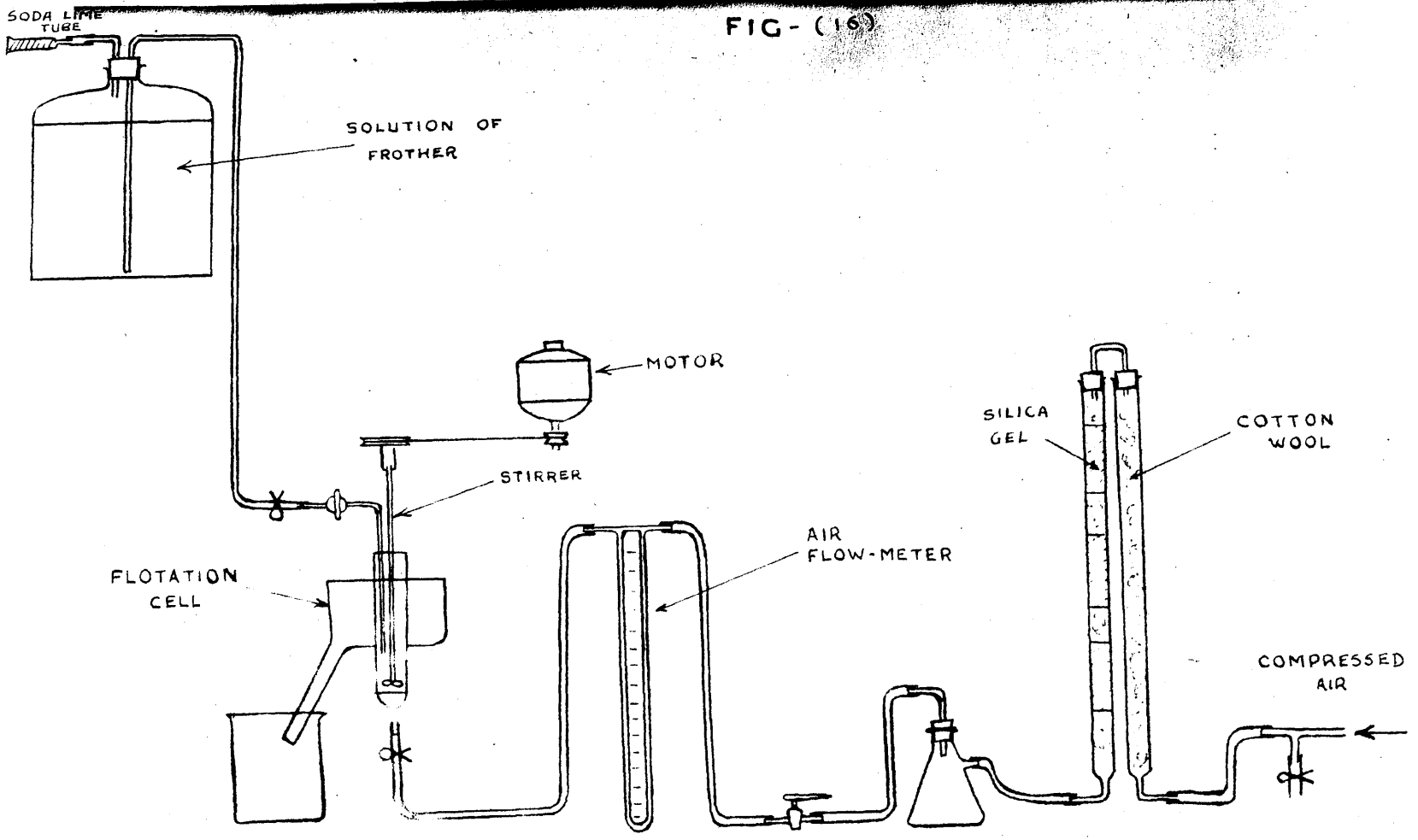
TERPINEOL SOLUTIONS



was measured by means of a measuring cylinder placed under the delivery tube below the cup. The air flow was then increased in steps of 4 cms. flowmeter reading and the volume of overflow was taken at each rate. The overflow volume is plotted against the air flow rate as shown in Fig. (15) from which it can be seen that 10 cms. flowmeter reading or 0.75 l./min. of air flow is just right for a flotation test as above this large bubbles tend to form reducing the stability of the froth and below this value frothing is not very satisfactory. Fig. (15), also indicates that the concentration of terpineol must be below 0.76 gms./litre to give a stable froth. All the three solutions started to overflow at the same air-flow rate of 0.32 l./min.

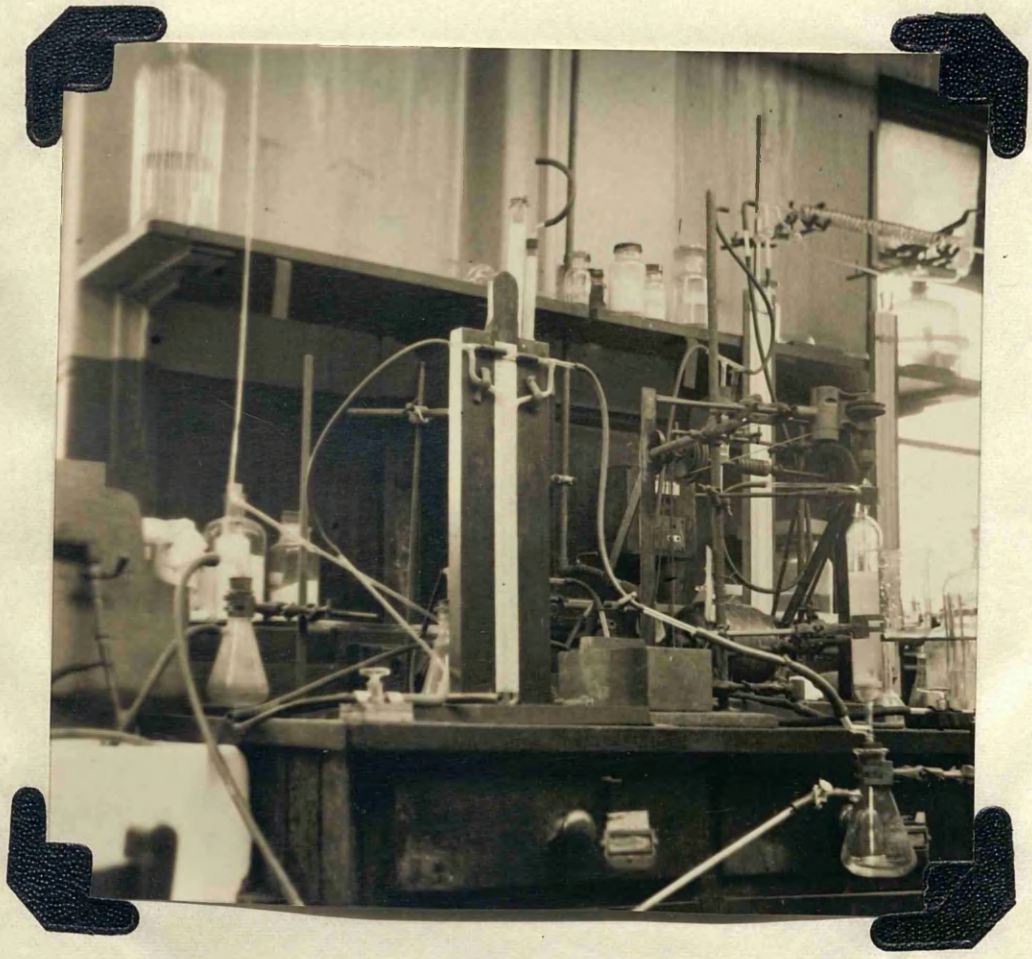
Again, 2-2½ cc. per minute rate of the feeding the solution into the cell to replace that lost in the overflow, as done by Knoll and Leaf, was too small a rate for those solutions which possess good frothing property. It was found that to keep the junction between the froth and the liquid in the cell constant, the volume rate of flow of "overhead" solution feed is generally higher than 5 cc. per minute sometimes rising to about 20 to 30 cc. per minute - in the case of soap solutions. An attempt was made to design a constant overflow device with the basic idea of balancing automatically the solution levels in the cell with a constant level apparatus. It failed to give the desired effect, because of the air bubbles travelling up the liquid delivery tube against the small liquid head, and the tendency of the solid particles to block up the opening immersed in the solution. The

FIG - (16)



FLOTATION UNIT

PLATE (I)



FLOTATION UNIT

(with new flotation cell)

difficulties were minimised by drawing out the tip of the glass tube to about 2 mm. in diameter and bending it to about 20° above the horizontal.

The set-up of the first flotation unit is essentially the same as that shown in Fig. (16) and in Plate I except that a separating funnel of about 300 cc. capacity was used to contain the frother solution to be fed into the cell during flotation and wash-bottles containing caustic soda solution and soda lime were placed in the air line to remove carbon dioxide and moisture respectively from the air. The later arrangement was later found to be unnecessary since cotton-wool and silica-gel columns were sufficiently effective in removing grease and moisture from air. Carbon dioxide in the atmosphere has practically no influence on flotation with organic acids. The air flow was regulated by a notched stop-cock and an initial regulation of air flow was achieved by means of an exhaust tube fitted with a screw-clip.

In all flotation tests, 15 gms. of ore and 75 cc. of the solution to be tested were added to the cell thus having a constant solid-liquid ratio of 1:5. The air flow was 0.75 l./min., as stated above, and the duration of flotation was timed for 5 minutes from the beginning of the overflow. For most solutions, the flotation is over within a period of $1\frac{1}{2}$ to 2 minutes after which the majority of the particles floated are carried up by entrainment. A conditioning time of three minutes in which the mineral was thoroughly mixed with the test solution by stirring, was allowed before the test.

In the first few tests 15 gms. of ore were weighed

out from a sample that had been dried in a vacuum oven and stored in a vacuum dessicator. Later a better and a less involved procedure was adopted. About 6.6 cc. of wet purified ore, stored under water, were measured out in a 25 cc. measuring cylinder and added to the cell. This volume was found to contain about 13 to 16 gms. of dry barytes. The small variations in the weight of barytes cause little change in pulp density and so it was considered to have little or no effect on flotation results. Care was taken to clean the beaker and the measuring cylinder, used for transferring barytes to the cell, thoroughly with chromic-sulphuric acid mixture.

In the presence of relatively coarse particles such as those of 120-150 mesh barytes, the frothing power of the frother solution was lowered to an appreciable extent. Although fine particles, below say 300 mesh size, stabilise the froth, the collision of the coarser particles with air bubbles leads only to the destruction of the froth. This is most noticeable when the solution has a low collecting power. On floating with solutions of the lower acids, it was found that the initial rate of air flow required to form a froth was higher with the solid present than when only the solution containing the reagents was used. Secondly, constant stirring of the pulp was necessary to keep the quickly settling mineral powders in suspension. The frothing of the solution was very much improved when stirring was introduced. A clean glass rod was used for stirring by hand in the first few tests. Later

TABLE (5)

Reproducibility of Results.

Collector	Concⁿ.	Temp. °C.	% Floated	Overflow Liquid gm./gm. of Solid.
n.Butyric Acid	10 gm./l. (112 lb/ton)	14.3	17.1	28.1
		15.5	16.1	29.6
		20.4	24.4	21.3
		21.0	18.2	28.6
		17.0	16.7	22.2
n.Caproic Acid	0.3 lb/ton	17.0	38.2	8.1
		17.0	37.4	6.95
		17.5	38.2	7.05

this was replaced by a glass stirrer rotated at 560 r.p.m. by means of a D.C. electric motor of 1/6 H.P. as shown in Fig. (16).

Reproducibility of Results.

From the figures in Table (5), it can be seen that the results are fairly reproducible even with a poor collector like n-butyric acid. The results incline to be irregular with poor collectors but as the collecting action improves better reproducibility is achieved. The figures for n-caproic acid shows only about 1.2 per cent. variation from the mean. It must be admitted that these values are rather high for 0.3 lb./ton caproic acid owing to incidental contamination by foreign impurities. Remarkably close values were obtained when soap collectors were employed with efficient agitation provided by the mechanical stirrer. The maximum deviation of the mean in all experiments was found to be $\pm$ 5 per cent..

Effect of Sintered Disc.

Apparently the porosity and the average diameter of the pores of the sintered disc seem to influence the flotation. This was discovered when a new cell of the same type was substituted for the first cell which was sent for repair. The flotation tests on 120-150 mesh barytes with n-valeric acid solutions were repeated and it was found that the percentage of barytes floated at each concentration of acid was lower than the value obtained with the first cell as shown in Fig. (17).

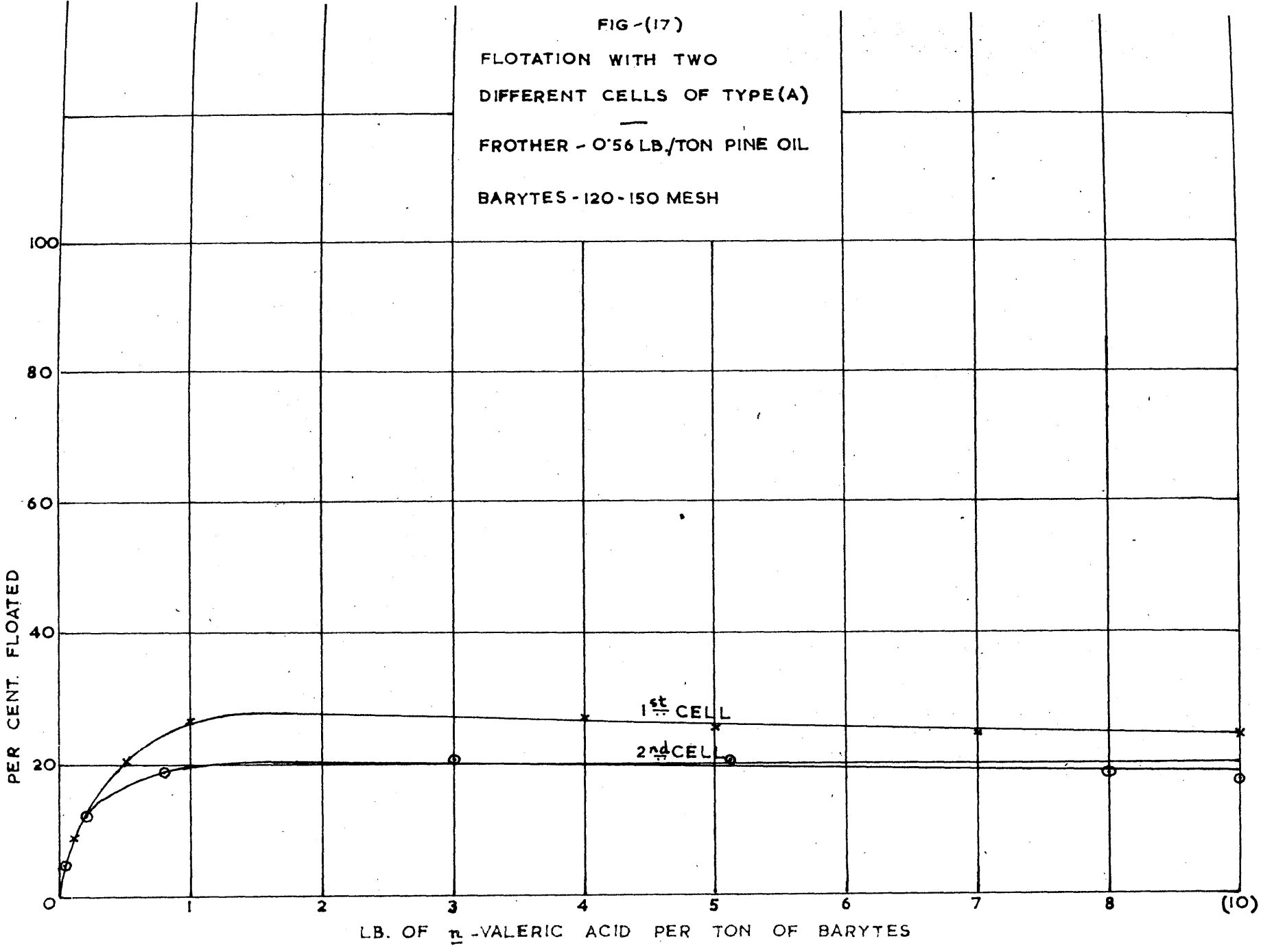
The two cells differ only in that the frothing tube of the second cell is about 1.5 cm. higher than that of the

FIG-(17)

FLOTATION WITH TWO DIFFERENT CELLS OF TYPE(A)

FROTHER - 0·56 LB./TON PINE OIL

BARYTES - 120-150 MESH



first one and that the sintered disc of the second cell allows an easy flow to water while a liquid can flow through the first cell only at a very slow rate. The latter is the more probable cause of the low results since the smaller pores of the first cell lead to a finer subdivision of air bubbles with the result that a greater volume of froth is produced at the same rate of air flow. Where a poor collector like n-valeric acid is concerned, the volume of froth will have a substantial effect on the percentage floated because of the increase in entrainment of particles with the production of more froth.

Flotation Cell (B).

In the case of the cell just described, 20 cc. of water measured out in a pipette had to be used to wash down the solids left in the outer cup into the overflow receiver. This caused a lot of inconvenience as the cell had to be removed from its position while care was taken not to lose any solid in the cup. The apparatus was simplified by doing away with the outer vessel and shaping the mouth of the tube in such a way that the froth could flow over from one side only. The details of the cell, designated (B), are given in Fig. (14). The top portion is simply blown into a bulb and cut away at an angle, widening the lip slightly to allow an easy path for the overflow.

This new cell was provided with a sintered disc of the same porosity as that of the old cell and it worked satisfactorily even with the soap solutions which give voluminous

froth. The only trouble with it was that the overflow liquid tended to go round the lip and flow down the side of the tube. This was avoided by extending the lip slightly forward and putting the receiving beaker so that it touches the cell without leaving a gap in between.

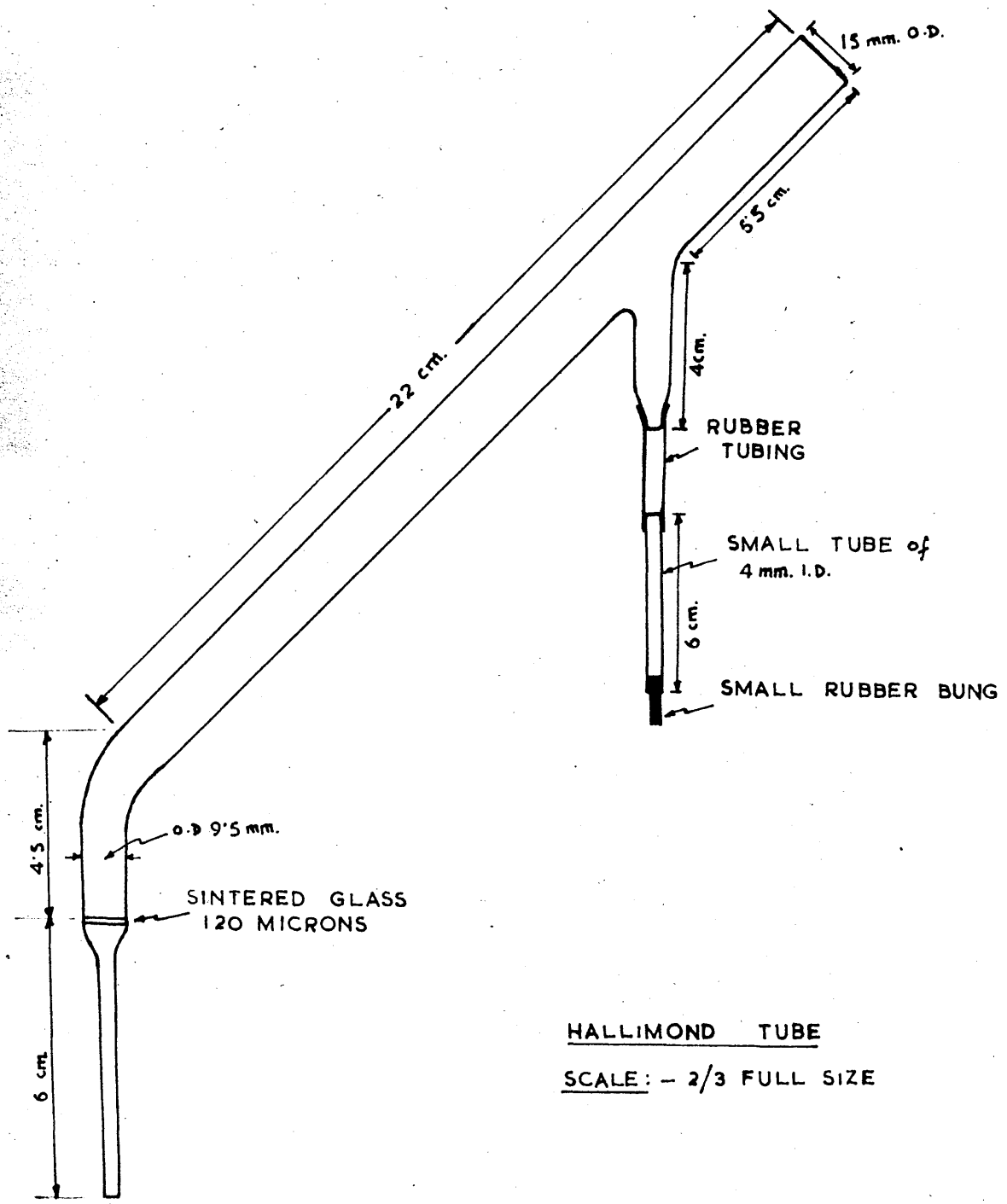
A thorough comparison of these two types of cells has not been made as it was considered to be unnecessary. From the similarity in almost every respect, one would expect their flotation results to be the same. This was proved to be true by the curves for the change in recovery with time, given in Fig. (20) of Chapter (VI).

Hallimond Tube.

A diagram of the Hallimond tube employed together with its dimensions is drawn in Fig. (18). The only difference between it and Hallimond's original tube (48) is the use of a sintered glass disc instead of a pad of cotton-wool as diaphragm. Hallimond recommended 60-90 mesh to 1 in. as a convenient size of ore placed to a depth not exceeding ½ in. above the pad. The sintered disc has the advantage of being suitable for finer particles and it does not need to be removed like cotton-wool after a series of tests. Moreover, as it is made of glass it can be cleaned thoroughly with chromic acid-sulphuric acid mixtures.

The lay-out of the apparatus used is given in Fig.(19). The air supply for the tube came from the exhaust side of an oil-rotary vacuum pump via two cotton-wool columns which removed grease impurities and dust. On the other hand,

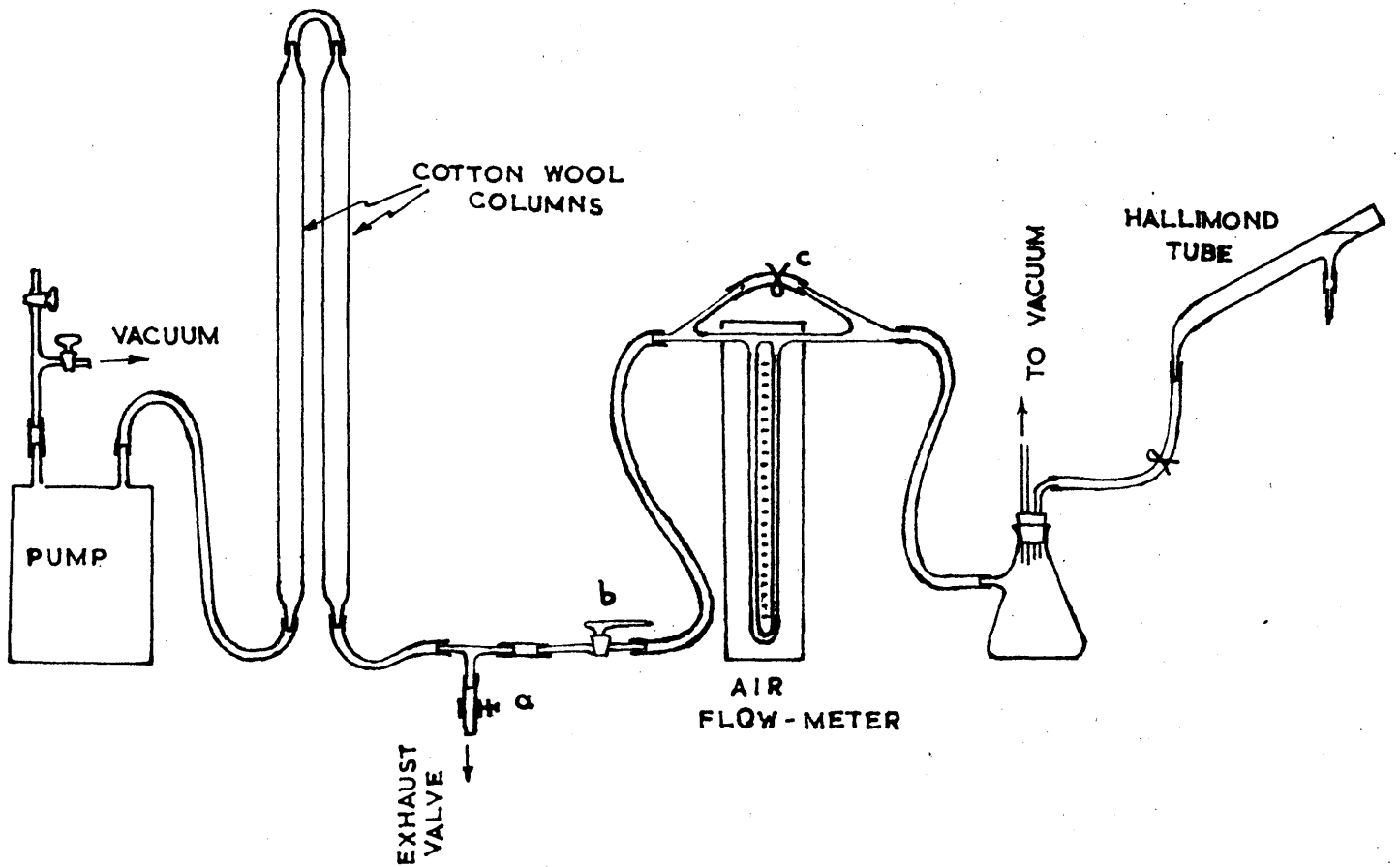
FIG - (18)



HALLIMOND TUBE

SCALE: – 2/3 FULL SIZE

FIG- (19)


COTTON WOOL
COLUMNS
VACUUM
PUMP
b
c
a
EXHAUST
VALVE
AIR
FLOW-METER
TO VACUUM
HALLIMOND
TUBE

the vacuum required for removing liquid from the tube was obtained from the vacuum side connected to a conical flask of 1 litre capacity. A rough adjustment of the air flow through the flowmeter could be made by controlling the screw-clip (a); the notched stop-cock (b) was for fine adjustment. When the flowmeter was not in use, the screw-clip (c) in the by-pass was always opened to prevent the flowmeter liquid from being blown away by excessive air pressure or suction. The rate of air flow used in all the tests was 4 l./hr.. Gentle bubbling action is required without any froth formation.

When air is passed into the tube, the air bubbles produced carry up the floatable particles along the upper wall of the tube to the liquid surface where they collapse releasing the particles. Because of the inclination of the tube, the released particles mostly fall into the small side tube or on to the glass wall above it from which they eventually enter the small side tube. The uncollected particles fall back to the bottom of the tube from which they are picked up again by air bubbles. The use of only a small quantity of ore is probably the reason for not needing a large air surface such as is provided by a frother.

The total volume of the main tube plus the small side tube was 45 cc. but 40 cc. of the collector solution was added to the tube for each test. Time of flotation was 5 minutes although the flotation was complete in a matter of about half a minute in most cases. When flotation was complete the small receiving tube was tapped until no more particles are left in the portion above it. It was then removed and tapped

again on a bench about three or four times. The height of the mineral particles in the tube on top of the small rubber plug was measured in mms., and expressed as a percentage of the height of the total powder. After removal of the liquid already tested, the floated solid was returned to the main tube by pointing the opened side-arm upwards, removing the rubber plug from the small tube and blowing the solid out into the main tube by a jet of distilled water. During the flotation it was found better to rotate the tube slightly in order to create an agitation of the powder bed. The proportionality of the height of the bed in the small side tube to the weight of the powder was verified by drying and weighing different depths of wet powder in the small tube.

Three definite advantages can be assigned to the Hallimond Tube. They are:-

(1) No frother is required. This is the only laboratory apparatus with which the collector solution alone can be used for flotation tests. There are some large machines, as for example that of Goyder and Laughton (49) that are capable of operating without the use of a froth.

(2) Only about 0.5 to 1 gm. of the ore sample is sufficient for a whole series of tests. For example, to investigate the variation in per cent. floated with concentration of a collector, one can start with the lowest concentration and the same sample can be used again and again with increasing concentrations. The accuracy of each determination was about 5%.

(3) Each test takes approximately 15 minutes. This is much quicker than any other laboratory method known.

The author has found the Hallimond Tube to be very useful for testing the presence of a collector coating on a sample of ore. If there is such a coating, flotation with distilled water should give an appreciable recovery.

.....

FLOTATION TESTS.

Chapter VI.

Flotation Variables.

A metallurgist operating a flotation mill has to contend with two types of flotation variables, those which can be controlled and those which cannot be controlled. For instance, the characteristics of the ore and the mill-water available are variables over which he has no control while other factors such as the pH of solutions, temperature, and pulp density can be easily standardised.

Although, in the case of a flotation plant, as many as twenty to thirty variables can be cited as belonging to these two headings, the number can be reduced to about nine in the case of a laboratory flotation test in a given cell with pure minerals of known composition. They are:

1) ... Concentration of frother,
2) ... Concentration of collector,
3) ... Concentration of activator, depressant, or other inorganic reagent,
4) ... pH of solution in the cell,
5) ... Temperature,
6) ... Time of collection of floated ore,
7) ... Pulp density,
8) ... Rate of air flow or other dimensional characteristics of cell, i.e., speed of rotation of stirrer, capacity of cell, etc.,

The obvious way to a systematic study of the flotation of an ore is to take one variable at a time while keeping the others under rigid control. This procedure is adopted in the investigations described below, but it must be remarked that the ideal conditions cannot be achieved simply because it is well-nigh impossible to impose a strictly rigid control over some of the variables. Thus, minerals can rarely be obtained entirely free from impurities which when finely ground, tend to give rise to soluble salts; no sizing method is capable of yielding particles of exactly uniform size; the pH value is difficult to maintain absolutely constant because of reactions between the mineral and air or carbon dioxide and water.

In this work we are particularly interested in the collector and its associated ionic atmosphere in the vicinity of the mineral surface, i.e., variables Nos. 2, 3, and 4. In an attempt, therefore, to obtain the optimum conditions under which to study these variables a number of preliminary tests were carried out. These were designed to eliminate, as far as possible, the effect of subsidiary variables, numbers 1, and 5 to 9 inclusive. The following experimental portion is divided into three sections, viz.:-

a) ... Preliminary tests,

b) ... Tests with fatty acids and their soaps,(i.e., variables Nos. 2 and 4 above)

c) ... Tests to show the effect of foreign anions and cations on the flotation. (i.e., variable No. 3)

Preliminary Tests.

Purification and Purity of Barytes.

Barytes was received in the form of fairly large pieces with patches of reddish brown iron oxide and greyish coloured earthy impurities. Only those pieces, having very little or no colouration on the surface, were taken and broken down to below 25 B.S.S. mesh in a clean iron mortar. Further size reduction was done in a Laboratory Raymond Mill.

The first stock of mineral was prepared by sieving the ground ore through 120 and 150 mesh screens. -120+150 mesh and under 150 mesh sizes were retained for use in both the adsorption experiments and flotation tests. Hand-sieving and the use of two close screen sizes were done in order to obtain particles of approximately uniform size free from fine particles as far as possible. As only about 10 per cent. of the total ground ore was retained on the 150 mesh screen while about 60 per cent. passed through it, it was decided to adopt a somewhat greater size range, viz., 130-300 B.S.S., for the next lot of barytes. In this manner a larger quantity of ore was made available for use. This was justified, where comparison of flotation results for these two different size fractions was concerned, for the specific surface and particle size of the 130-300 mesh size were almost of the same order as those of the 120-150 mesh, as shown below.

	Average Surface Area (cm^2./gm.) Rigden's Method	Lea & Nurse Meth.	Particle Size microns
120-150 mesh -	794.5	632.4	150 microns
130-300 mesh -	750.4	542.0	134 microns

The first step in purification was to wash the ground ore repeatedly with hot tap water. The dirt, slimes and soluble impurities were thus removed. It was then treated with hot concentrated hydrochloric acid until no more iron was detected in supernatent liquid. Then the acid was removed by washing several times with warm distilled water. The wash water was tested with Silver Nitrate to ensure that no chloride remained with the ore. To remove grease on the mineral surface washings were continued with the following solvents in the order; absolute alcohol, ether, and absolute alcohol. Finally distilled water was used to remove the alcohol.

Every purified specimen was tested for acid or alkaline impurities by taking the pH of the filtrate from a pulp made up of 15 gms. of ore and 75 cc. of distilled water. The pH of distilled water in our laboratory varied from 5.12 to 5.90. Only in one case was a change in pH observed. A further washing with distilled water removed the traces of acid the presence of which was indicated by the decrease in pH of 0.26 obtained with that sample.

-120+150 mesh barytes, which was prepared from pieces entirely free from any coloration, was found to have the following composition by spectroscopic analysis:-

Constituent.	Per Cent.
Pure Barium Sulphate....	94.5
Silica	1.0
Calcium	1.0
Copper	1.0

Magnesium	1.0
Strontium	1.0
Tin	1.0
Aluminium, Lead, Zinc, Sodium	..... 0.01 to 0.1 (traces)
Iron	..... less than 0.01 (mere traces)

On the other hand, since -130+300 mesh barytes was prepared from pieces showing some colouration due to iron, the two samples of this mesh size were found to contain 0.34 per cent. and 0.15 per cent. of iron. This was determined with potassium thiocyanate even after all the care taken in leaching with hydrochloric acid. The included iron was removable only after grinding to a very fine state. No spectroscopic analysis was done for these samples as it was considered unnecessary.

(1) Flotation with Frothers Only.

The frothing agents used in the flotation tests were pine oil and terpineol. The former was used in the first few series of tests with lower members of the acid homologues at a time when terpineol was not available.

Pine oil is one of the most widely used frothers in froth flotation. It is obtained as a pale yellow oil from various species of the pine, either by steam distillation or by dry distillation. The sample used was kindly supplied by Messrs. Macneill and Sloan Ltd. and was designated,

"Steam distilled Pine Oil (High Grade)".

The physical constants of this pine oil were:-

Density - $D_4^{20^\circ}$ = 0.9272

Refractive Index - $n_D^{20^\circ}$ = 1.4830

Specific Rotation α^{20° = +8.98

Boiling Range = 200° - 220°C.

Terpineol, which is the chief component of pine oil, has been widely used in flotation experiments as a 'standard' frother. Taggart, Taylor and Ince (50), in their large classification of flotation agents, class Terpineol as 'excellent'. Gibb (28) has shown, from his studies on the frothing properties of pine oil and its constituents, that terpineol possesses a greater frothing power than pine oil.

It has been found that most frothers also possess collecting properties if used above a certain threshold concentration and within a definite range of pH values. Pine oil and terpineol both fall within this category. It was, therefore, decided to find out whether these reagents have any appreciable effect on flotation of barytes at the respective concentrations to be employed in the subsequent tests. Using 0.05 gm. per litre (0.56 lb./ton) solution of pine oil and 0.0447 gm. per litre (0.50 lb./ton) solution of terpineol at their pH values of 5.47 and 5.68 respectively, flotation tests gave less than 2 per cent. recovery for both solutions. As this was considered negligible, no correction was made for the effect of frothing agents in the tests described later.

The pH factor was not investigated for the reasons that (1) the flotation results are approximate and are, in general, for comparative purposes and (2) that the pH values of the solutions are controlled in most instances.

(5) Temperature.

All flotation tests were carried out at room temperature which remained mostly between 15° to 25°C during the year. The maximum variation during a day is about 5°C and within this small range no indication of any change in flotation with temperature was noticed. Consequently, it was decided to ignore the influence of temperature on the flotation of barytes.

(6) Time of Collection of Floated Ore.

130-300 mesh barytes was floated with 0.05 lb. of sodium laurate per ton of ore (0.0045 gm. per litre) and the overflow was collected over different time intervals. This was done with both cells, A and B. The cumulative per cent. floated was plotted against time in minutes as in Fig. (20). The curves for the corresponding rate of flotation in gms. of barytes per minute, and the rate at which liquid was taken over in the floated pulp by 1 gm. of solid, are also included. The average time intervals are referred to in the last two instances.

As a comparison between the two cells has already been made in the chapter on flotation cells, only an interpretation of the various curves in Fig. (20), in respect of the time factor, will be made here. It can be seen that

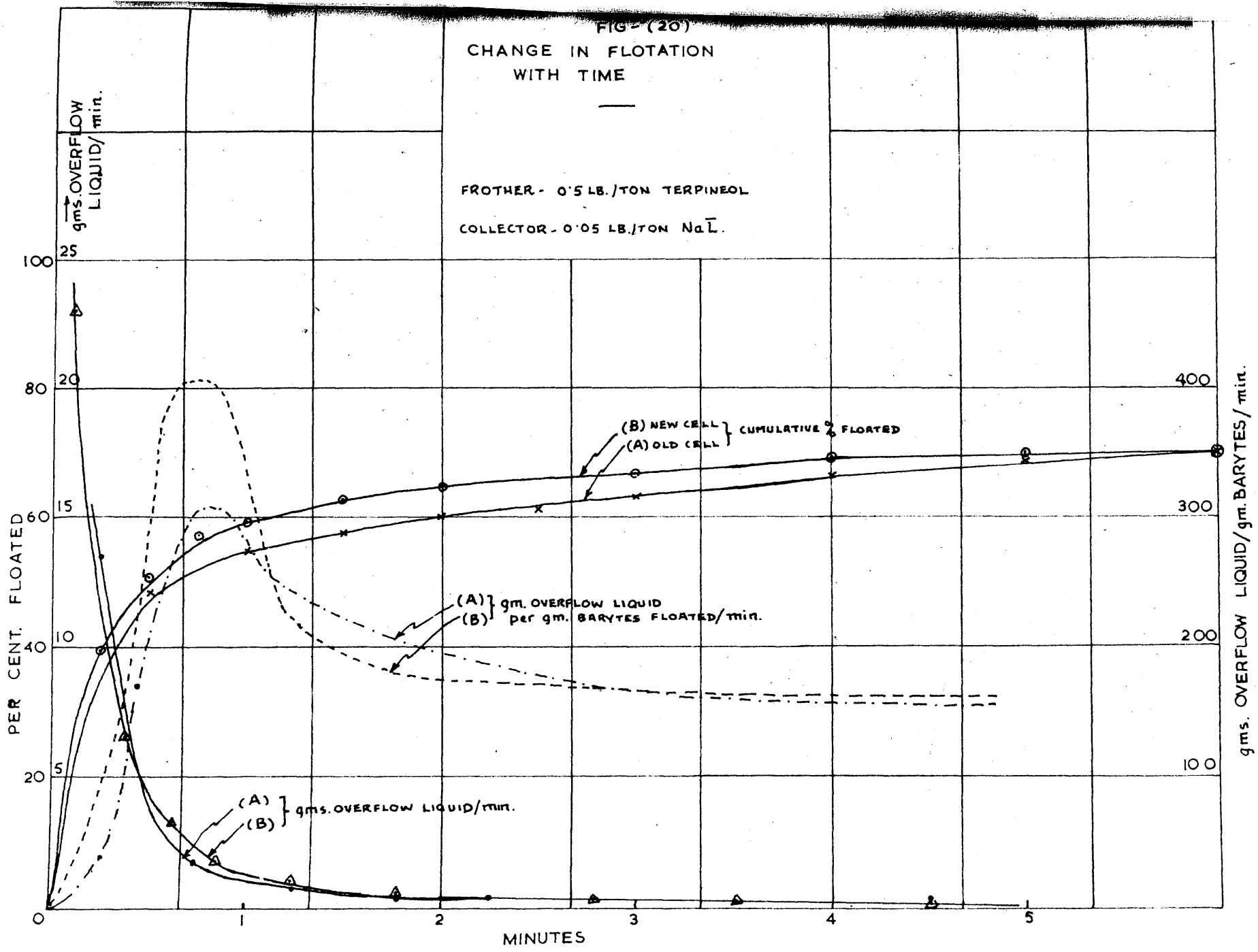


FIG - (20)
CHANGE IN FLOTATION WITH TIME
FROTHER - 0·5 LB./TON TERPINEOL
COLLECTOR - 0·05 LB./TON NaL.
gms. OVERFLOW LIQUID/min.
PER CENT. FLOATED
gms. OVERFLOW LIQUID/gm. BARYTES/min.
MINUTES
(B) NEW CELL
(A) OLD CELL
CUMULATIVE % FLOATED
(A)
(B)
gm. OVERFLOW LIQUID per gm. BARYTES FLOATED/min.
(A)
(B)
gms. OVERFLOW LIQUID/min.

the cumulative per cent. floated rises sharply at first to become almost constant after an interval of about 4 minutes from the beginning of the test. The rate of flotation, i.e., gms. overflow liquid per minute reaches a constant value after two minutes, the small rate beyond that time being considered as due to mechanical entrainment by the froth. These conclusions indicate that the bubble-mineral attachment of floatable particles is complete in a matter of three to four minutes and they also justify the adoption of five minutes as time of flotation. The decrease in flotation rate in the first minute is evidently more than 20 gms. of overflow liquid per minute. As the flotation rate drops, the rate of overflow of liquid per gm. of solid in the overflow (i.e., gms. overflow liquid/gm. barytes floated/min.; dotted curves in Fig. (20)) increases to maximum which occurs at approximately the same time as the point at which the constant flotation rate starts. The rate of liquid overflow per gm. of barytes then declines to reach a constant value after about 2 to 3 minutes. This can be explained by the decrease in weight of ore floated while the weight of liquid overflow remains nearly the same. The latter then decreased when the frothing effect of the soap plus terpineol was being replaced by that of terpineol alone. Similar conclusions were arrived at by Schumann (51) in his study on "Flotation Kinetics" with a copper ore.

(7) Pulp Density.

Different pulp densities were obtained by adding

to the cell different volumes of wet ore (130-300 mesh) measured out in a 25 cc. measuring cylinder followed by 75 cc. of 0.0027 gm./l. sodium laurate solution. This concentration of soap was chosen because it gives about 60 per cent. recovery with the usual pulp density of 1.11 (75 cc. of solution to 15 gm. of ore) thus providing a margin for either an increase or a decrease in recovery.

The pulp density was calculated from a knowledge of the weight of dry ore in the cell, its density and the volume of the solution added. Because the solution was very dilute its density was taken as equal to that of water.

Thus, pulp density = $\frac{\text{gms. of solid + gms. of liquid}}{\text{Total volume (in ccs.)}}$

in this case. For practical purposes, i.e., in industry, the pulp density is the percentage of dry solid in the pulp i.e.

$$\text{pulp density} = \frac{\text{gms. solid}}{\text{gms. solid + gms. liquid.}} \times 100 \text{ per cent.}$$

For example, 15 gms. of solid with 75 cc. of solution here can be expressed as having a pulp density of either 16.7 per cent. or 1.10. The simplest way of reporting the amounts of solid and liquid in the pulp is by means of the pulp dilution ratio which is merely the ratio of the weight of ore to that of the liquid. Usual pulp dilution ratio employed is between 1:1 and 1:5 respectively.

In the present study, the concentration of collector in water was kept constant and so its concentration with respect to the mineral varied since different weights of solid

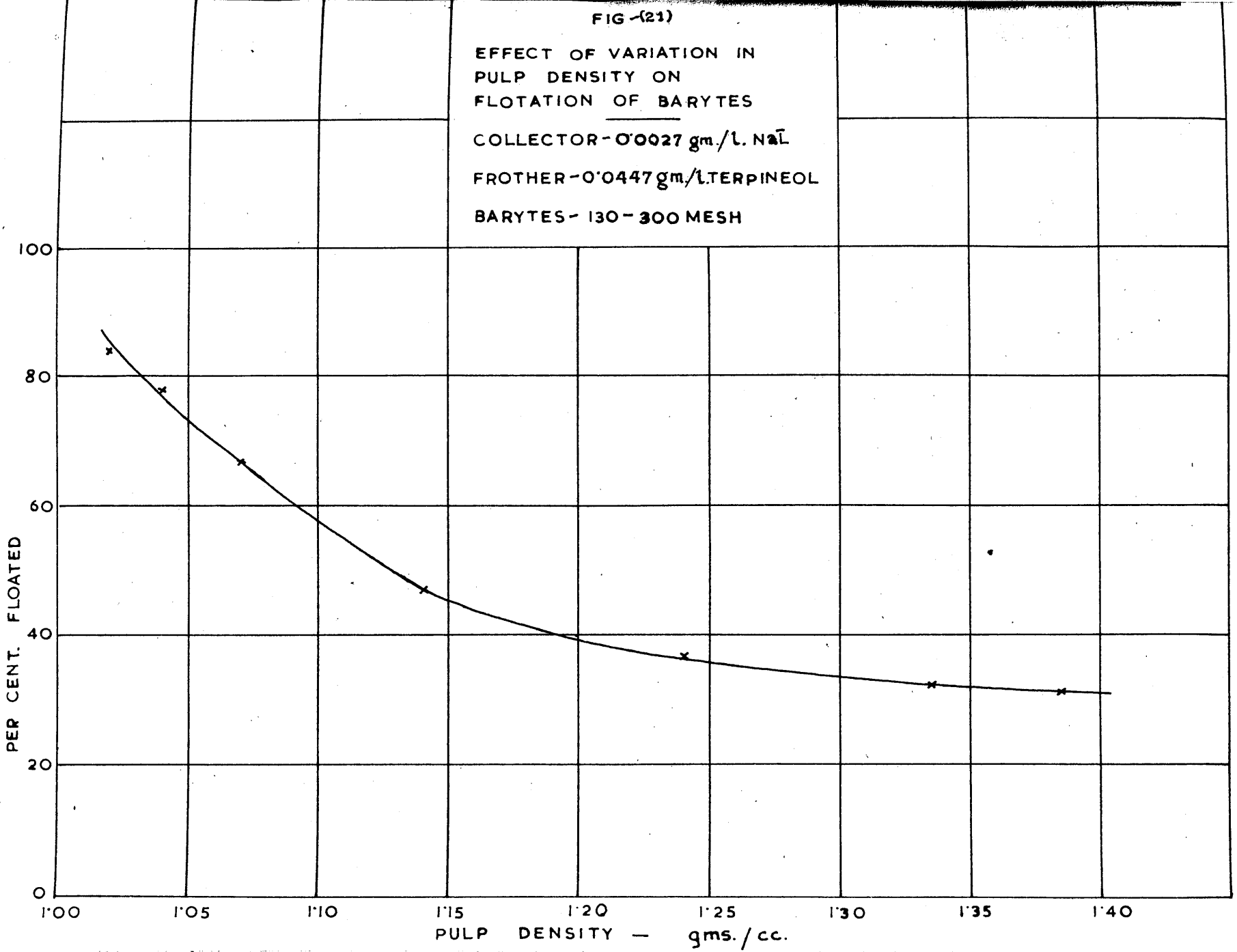
FIG -(21)

EFFECT OF VARIATION IN PULP DENSITY ON FLOTATION OF BARYTES

COLLECTOR - 0·0027 gm./l. NaL

FROTHER - 0·0447 gm./l. TERPINEOL

BARYTES - 130 - 300 MESH



were taken while the liquid volume was the same throughout. An alternative way was to keep the collector concentration with respect to the ore constant.

The results, given in Fig. (21), indicate that flotation decreases as the pulp density is increased until a constant value is attained at a recovery of about 30 per cent. and after a pulp density of 1.25, i.e. a pulp dilution ratio of 1 of solid to 3 of solution.

It is a deplorable fact that few data have been published in spite of the importance of pulp density factor. Fahrenwald, Newton and McManus (52) also found that when amyl xanthate concentration, with reference to the water, is maintained constant, the recovery of gold ore decreases with increase in pulp density.

Obviously the proportion of particles coated with the collector film will decrease with increase in weight of the ore in this particular case where the volume of liquid and the concentration of collector in solution are maintained constant. This may be responsible to some extent for the above behaviour.

Apparently, from Fig. (21), the best range of pulp density to work with, at least for sodium laurate solutions, is between 1.15 and 1.05. The latter density needs only about 7 gms. of ore to 75 cc. of solution. Below 1.05 the quantity of ore added is so small that the percentage carried over mechanically will be proportionately high compared to that due to the actual collecting action. Again, at

densities higher than 1.15, there is too much of ore present in the small cell and the result is that the collection is slow and the frothing power of the solution is reduced owing to the presence of a large mass of solid over the porous diaphram which causes the aggregation of small air bubbles to form large bubbles. Hence, the pulp density 1.14, used in the later tests, is a suitable value.

From economic point of view, pulp density is an important factor. Evidently, the greater the quantity of ore handled in each batch the more economic will the process be. The separation will, however, be poor since the capacity of each cell is constant and the pulp density will consequently be high with large quantities of ore. On the other hand, the recovery of 'useful' mineral will be high at high dilutions but as the input of the ore and the output of the 'useful' mineral are low the process will be less likely to pay. It is clear, therefore, that a happy medium must be chosen where largest possible quantity of ore is being handled and the highest recovery achieved.

At the moment, the choice of a suitable pulp density seems to be restricted to the usual empirical dilution ratios of 1:1 to 1:5 and a satisfactory value is only arrived at by carrying out preliminary tests and varying the pulp density within this range. If the fundamentals of flotation were understood, the correct amounts of the ore and the solutions could be worked out from a knowledge of the theoretical minimum concentrations of reagents required per unit weight

of ore and the capacity of the flotation cell.

(8) Rate of Air Flow.

The effect of rate of air flow on flotation of barytes was investigated by tests with 0.03 lb./ton sodium laurate solution and also with 0.5 lb./ton and 0.1 lb./ n-caprylic acid solutions. For sodium laurate solution, flotation cell (B), Fig. (14), was used with motor stirrer while for n-caprylic acid solutions the first flotation unit with stirring done by hand was used. The variations in recovery of barytes and the total weight of overflow liquid with air-flow rate are shown in Figs. (22) and (23).

From the results, a general conclusion can be drawn that there exists a narrow range of air-flow within which a constant recovery is possible. For n-caprylic acid that range is from 0.35 to 0.48 l./min. while for sodium laurate it is from 0.6 to 0.84 l./min.. This difference is probably due to the more efficient agitation applied to sodium laurate solution, which will result in the bubbles and particles having a higher kinetic energy and thus less liable to maintain contact. It will, therefore, require more air, i.e., froth, to collect a given weight of mineral. The greater weight of overflow liquid obtained with sodium laurate bears out this argument. The case of 0.1 lb./ton caprylic acid is that of a solution possessing a poor collecting action but much influenced by the increase in froth volume caused by the rise in air flow.

The upper limit of air flow is the point at which

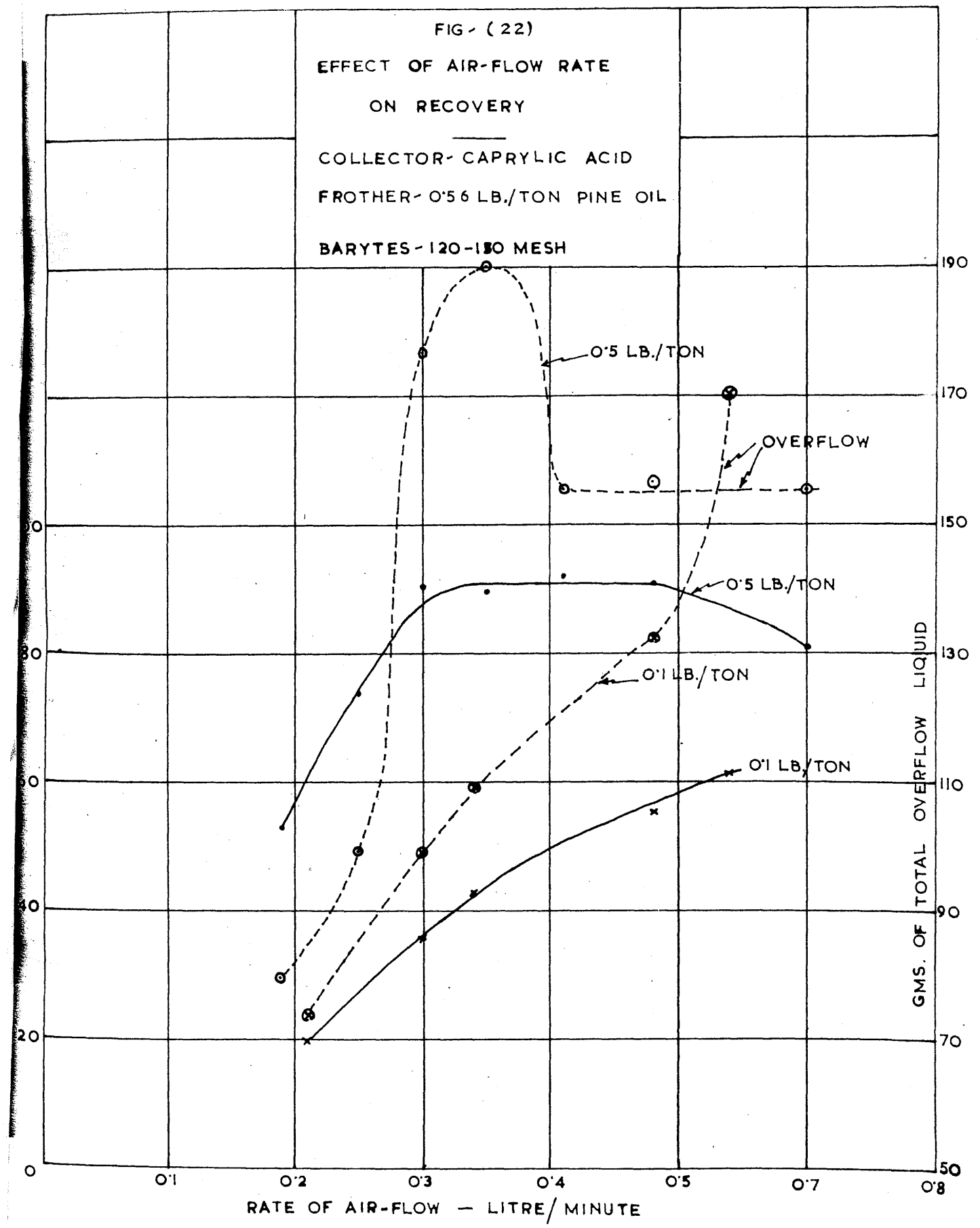
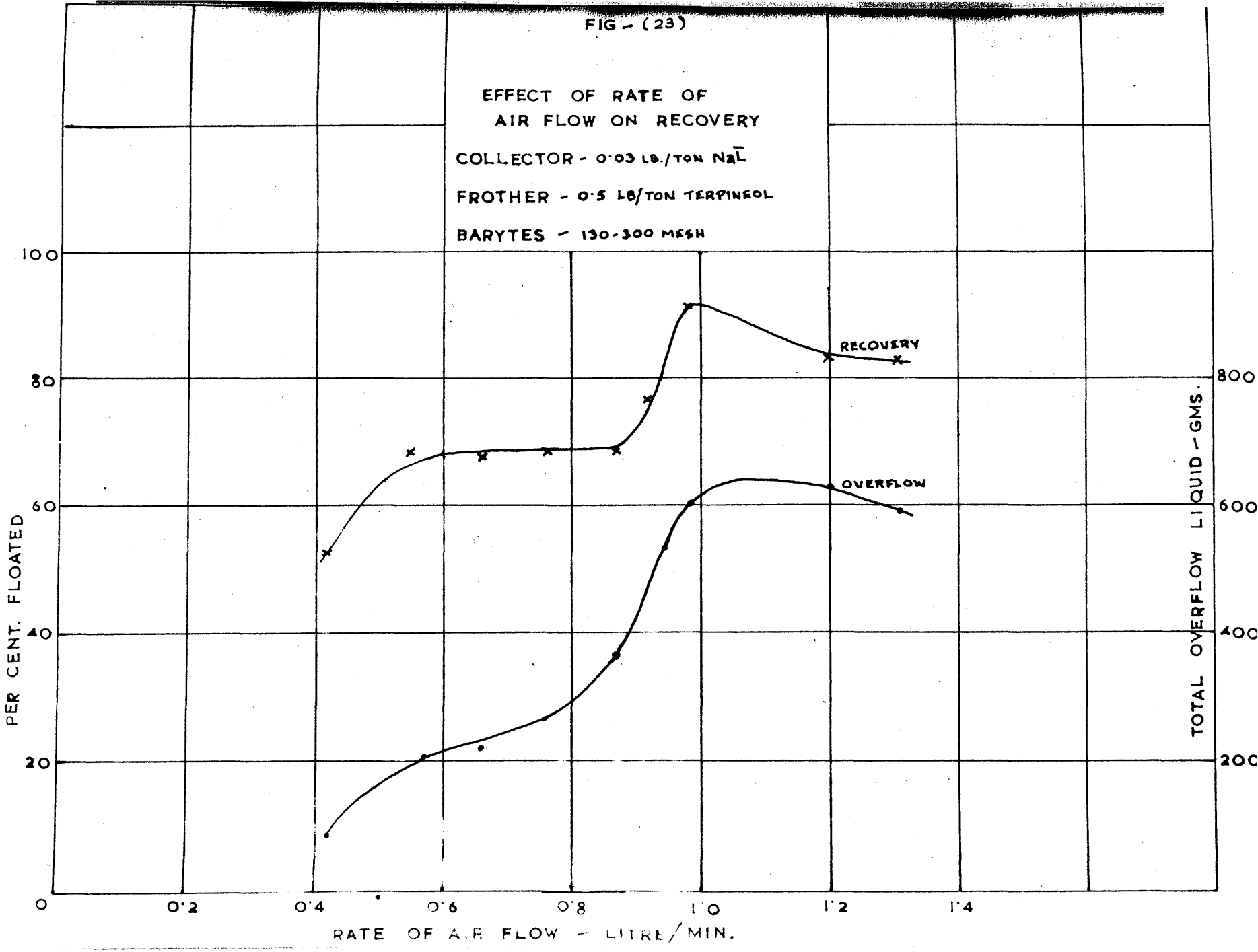


FIG - (22)
EFFECT OF AIR-FLOW RATE
ON RECOVERY
COLLECTOR - CAPRYLIC ACID
FROTHER - 0·56 LB./TON PINE OIL
BARYTES - 120-180 MESH
0·5 LB./TON
OVERFLOW
0·5 LB./TON
0·1 LB./TON
0·1 LB./TON
0
20
40
60
80
100
190
170
150
130
110
90
70
50
0·1
0·2
0·3
0·4
0·5
0·7
0·8
RATE OF AIR-FLOW — LITRE/MINUTE
GMS. OF TOTAL OVERFLOW LIQUID

FIG - (23)


EFFECT OF RATE OF AIR FLOW ON RECOVERY
COLLECTOR - 0·03 LB./TON NaL
FROTHER - 0·5 LB/TON TERPINEOL
BARYTES - 130-300 MESH
RECOVERY
OVERFLOW
PER CENT. FLOATED
TOTAL OVERFLOW LIQUID - GMS.
RATE OF AIR FLOW - LITRE/MIN.
0
20
40
60
80
100
200
400
600
800
0·2
0·4
0·6
0·8
1·0
1·2
1·4

the recovery begins to fall owing to the formation of large air bubbles. The effect of frothing on flotation is evident from the parallelism between the flotation and overflow curves. This is brought out more clearly by the second rise in percentage floated with air flow occurring simultaneously as the sharp increase in overflow liquid in the case of sodium laurate.

From a study of these curves and the characteristics of the cell and calibration of the flowmeter an air flow rate of 0.72 l./min. was taken as suitable and used in all the flotation tests. This is considered as a reasonable rate especially with the stirrer-motor arrangement.

(9) Particle Size.

Samples of barytes, screened to different B.S.S. mesh sizes, were deslimed and purified in the manner already described. They were then floated with 0.04 lb./ton sodium laurate solution. The average particle size of each sample floated was determined by measuring the dimensions of 50 particles under microscope. The results, given in Fig.(24) indicate:-

(1) That at less than -50+70 mesh or greater than 295 microns, barytes was practically unfloatable.

(2) That maximum floatability was reached at -200+300 mesh or 75 microns.

(3) That barytes must be ground to pass at least through 90 mesh to be floatable under the present conditions.

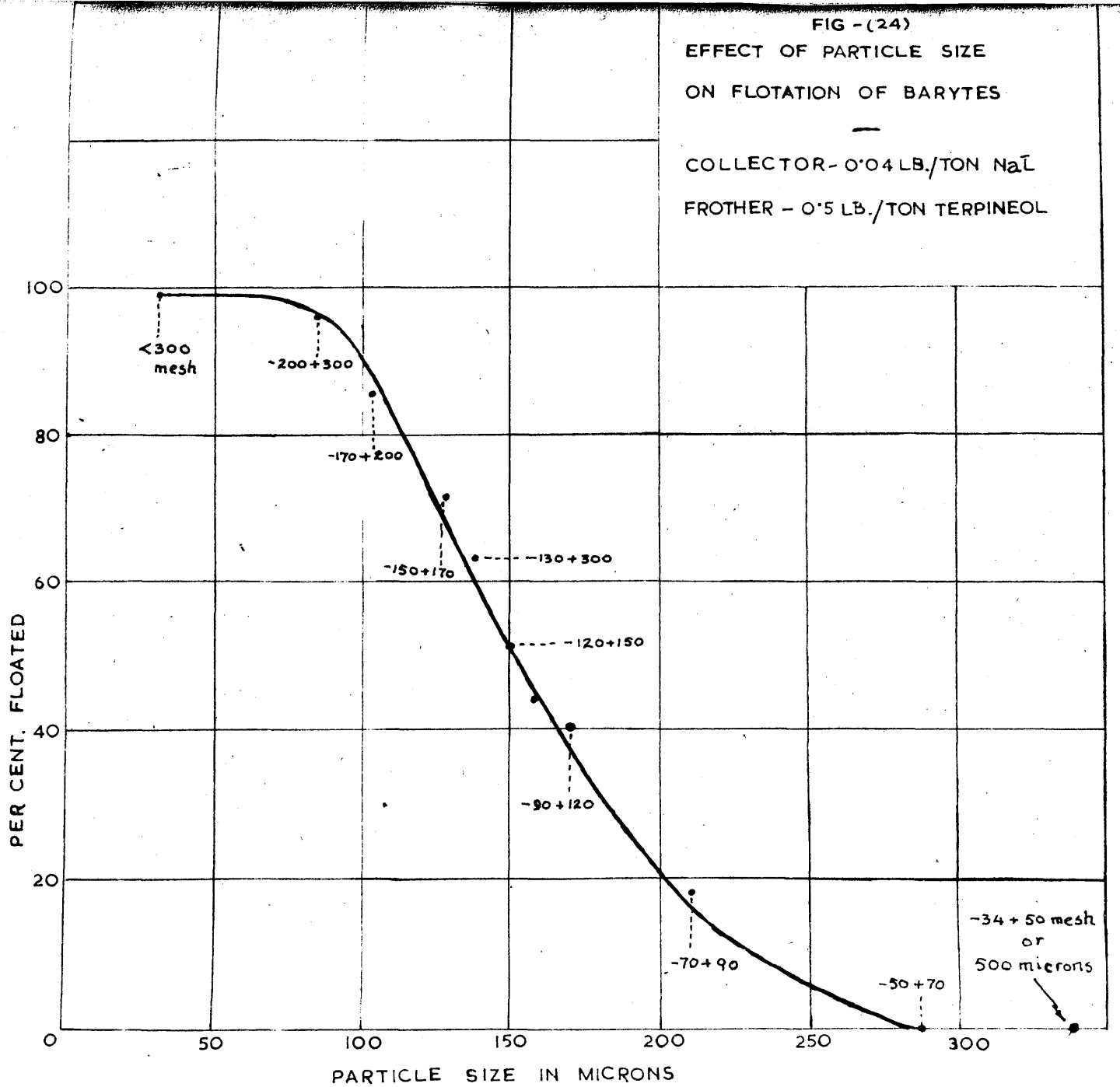
It was observed that particles of -34+50 mesh and

FIG - (24)

EFFECT OF PARTICLE SIZE ON FLOTATION OF BARYTES

COLLECTOR - 0·04 LB./TON NaĪ

FROTHER - 0·5 LB./TON TERPINEOL



-50+70 mesh sizes were so coarse that frothing was completely suppressed. Similar results were obtained by Keck, Eggleston and Lowry (53) while floating massive haematite with sodium oleate and terpineol. They found that haematite was unfloatable below 400 microns and that the flotation showed a maximum at 60 microns then decreasing with increasing fineness.

The recovery for 130-300 mesh barytes is about 10 per cent. higher than that for 120-150 sample. This may be attributed to the somewhat higher particle size of the former. It probably indicates that the flotation results for these two different mesh sizes can be compared although caution must be exercised paying due regard to possible variations in particle size and surface area from sample to sample.

.....

FLOTATION WITH FATTY ACIDS AND SOAPS.

Chapter VII.

Preparation of Solutions.

Wark (3) stressed the importance of specifying the method of preparation of solutions, particularly with regard to temperature and dilution changes, in describing flotation tests with solutions of compounds of high molecular weight. Micelle formation may affect the flotation results to a considerable extent. About fifty molecules constitute a micelle with the paraffin chains in the interior and the polar carboxyl or similar groups in the outer surface. The concentration at which micelle formation takes place is in the region of N/1000 or approximately 250 mg. per litre. Since the present concentrations of higher fatty acids and their soaps were not more than 40 mg. per litre the possibility of micelle formation is remote.

In actual plant practice the necessary quantities of reagents are added in a definite order into water in the flotation cell. Some investigators follow this procedure on the laboratory scale. In the present flotation tests, three different methods of preparation of solutions were used. With the soluble lower acids, a solution containing the frother and the maximum concentration of acid to be tested was made up and the lower concentrations were obtained by dilution of this solution with the frother solution. Either pine oil or terpineol was used as frother. The former was used only

when the latter was not available. Terpineol was preferred as it is the principle constituent of pine oil and is considered the 'true' frother in it. The frother concentrations were 0.56 lb./ton for pine oil and 0.5 lb./ton for terpineol respectively. These were chosen after a few preliminary tests with different concentrations of each frother in the flotation cell.

The soap solutions were prepared in a similar manner except that for the soaps of higher fatty acids, the terpineol solution had to be heated initially to about 70°C to allow easy solution of soap. The solution was then cooled and made up to the required volume. Secondly, where concentrations greater than 0.1 gm./l were required with the lower acids, different weights of acids were dissolved in 1 litre of the frother solution. Finally, for the higher fatty acids, which dissolve with great difficulty in water at room temperature, a solution of the acid in re-distilled methyl alcohol was first prepared and the necessary volume of this solution was then added to 75 cc. of the frother solution in the flotation cell by means of a microburette. The volume of methyl alcohol added did not exceed 1 cc. and this small volume was found to have little or no effect on the flotation of barytes. Probably an appreciable amount of the alcohol was evaporated away during the passage of air into solution in three minutes of conditioning time employed.

That care needs to be exercised in the choice of a suitable solvent for these higher acids was shown by the work

of Keck and Jasberg (54). In studying the flotation of gypsum with fatty acids, they found that ethyl alcohol was unsuitable because it increased flotation when used in quantities required for a solvent, 1cc. of alcohol being approximately equal to 32 lb. per ton. They also found that ethyl ether affected flotation to a great extent. They, however, used a constant quantity of 0.1 cc. of ethyl ether to dissolve different quantities of oleic acid so that the effect of the ether would be the same throughout. Alcoholic solutions of fatty acids were used by them in investigating the flotative properties of haematite and magnetite.

Effect of Mode of Preparation of Solutions.

In an attempt to discover if the recovery of mineral was affected by the mode of addition of collector to the cell, two series of flotation tests were carried out using sodium laurate as a collector and terpineol as frother. In Fig. (25) are shown the two curves obtained for the variation in percentage floated with concentration of sodium laurate. The points on the curve (a) were obtained by adding, with a micropipette, different volumes of 0.0089 g./l. sodium laurate solution to 75 cc. of terpineol solution (0.5 lb./ton) in the flotation cell, whereas the points in (b) were obtained by diluting successively the 0.89 gm./l. sodium laurate solution with 0.5 lb./ton terpineol solution. While the micropipette values at low concentrations are more likely to be in error due to difficulty in measuring out small volumes of liquids accurately, the regularity of the curve makes this appear

FIG-(29)

RECOVERY OF BARYTES AGAINST CONC^{N} OF COLLECTOR

BARYTES - 130-300 MESH.

FROTHER - 0·5 LB/TON TERPINEOL

COLLECTOR - SODIUM LAURATE

pH - 5·10

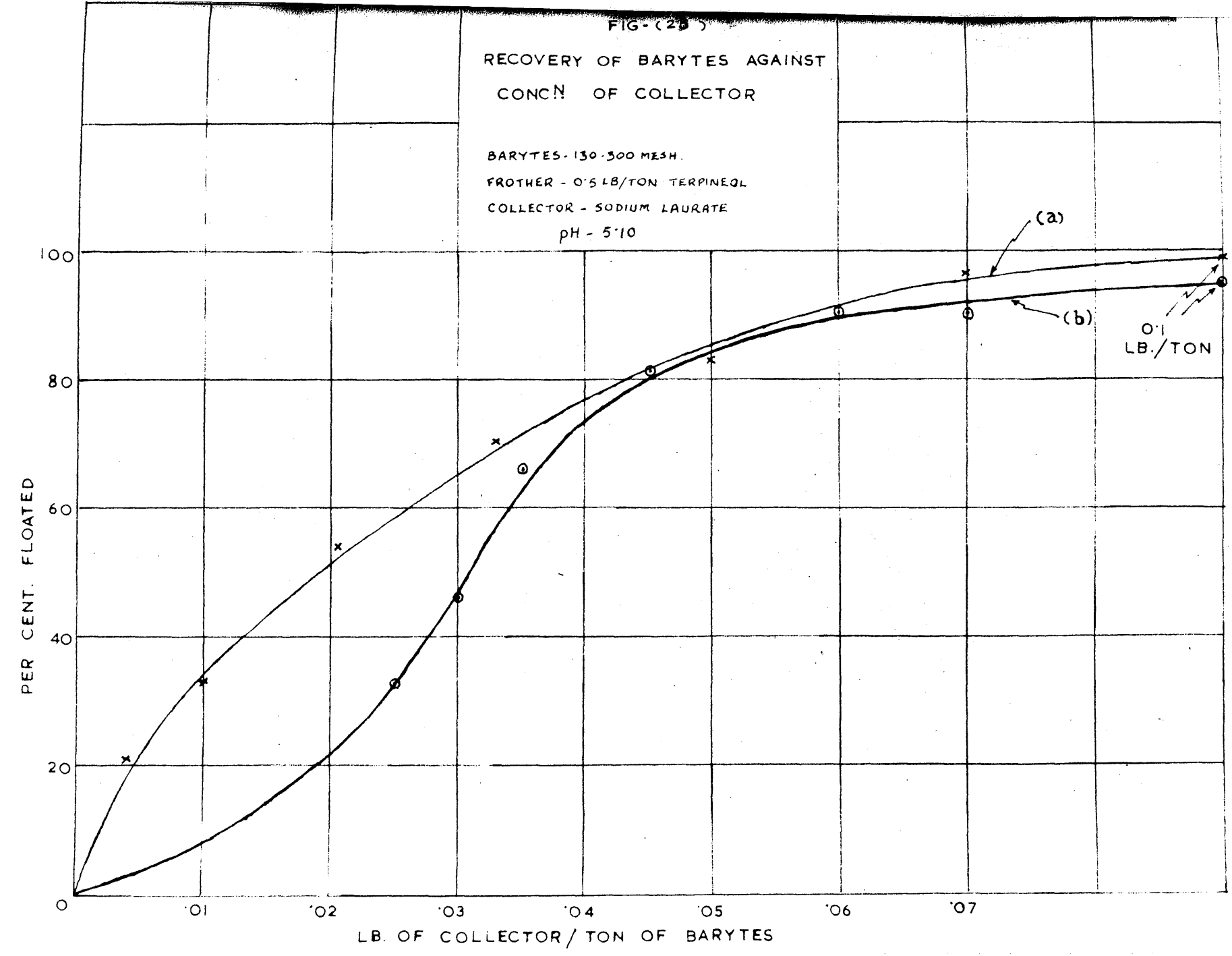


TABLE (6)

Days	Collector	Conc^{n}. lb./ton.	Room Temp.°C	pH.	Per Cent Floated.
1	Sodium	0.05	15.5	6.54	86.5
2	Laurate		17.0	6.10	82.0
3			17.0	5.97	78.6
4			18.0	6.02	68.3
9			18.0	6.24	18.4

TABLE (7)

Days	Collector	Conc^{n}. lb./ton.	Room Temp.°C	pH	Per Cent Floated.
1	Lauric	0.0025	10.0	6.40	51.2
2	Acid		17.0	6.33	50.0
3			17.0	6.30	51.0
4			18.0	6.27	36.0
9			18.0	6.11	17.6

unlikely. The micropipette method may result in momentary localised high fatty acid concentrations with increased adsorption and flotation. On the other hand, the diluted solutions of curve (b) are of necessity older than those of curve (a), i.e., the fatty acid molecules have been longer in contact with water, and the 'hydration' effect, which is shown below to reduce collecting power, will be more in evidence than in the case of solutions prepared in situ by means of the micropipette. Above a concentration of 0.04 lb./ton the mode of preparation of the solution appears to have little effect on recovery.

Effect of Age of Solutions.

It was soon discovered that the age of some of the collector solutions had an influence on the recovery. This is shown rather clearly by a series of tests carried out with a solution of sodium laurate (0.05 lb./ton ; pH = 6.54) and a series with a solution of lauric acid (0.0025 lb./ton; pH = 6.4). As shown in Table (6) and Table (7), the 86.5 per cent and 51.2 per cent. to 18.4 and 17.6 per cent respectively in 9 days. The pH of both solutions showed a negligible decrease of about 0.3. Their frothing power remained almost unaltered since the weight of overflow liquid collected in every test was over 200 gms.. A repetition of the test with freshly prepared solutions of the same strength gave similar initial recoveries thus removing any suspicion regarding the contamination of the ground ore which was always kept under distilled water. Renewal of the air purification system

did not improve the results. Having thus examined all possible sources of error, it was felt that the solutions must be undergoing some progressive change due to the atmosphere or to the water in which the reagents were dissolved.

On the other hand, however, there was a complete absence of any change in percentage of barytes floated in the case of 0.03 lb./ton sodium laurate solution at an alkaline pH of 10.4 and over a period of 4 days.

It appears that there must be some slow reaction taking place between the collector molecule, the water, and perhaps the dissolving gases from the atmosphere, i.e., oxygen, carbon dioxide, etc., which are progressively reducing the ability of the anion or fatty acid molecule to adsorb on the mineral surface. That this is not a mere hydrolysis is shown by the fact that lauric acid is affected quite as much as is sodium laurate. It is more probable that the laurate ion or lauric acid molecule has been partially oxidised or hydrated in some way by the large bulk of water in which it finds itself. Again, although we are well below the reported critical micellular concentration, it may be that in the long time of contact there are sufficient collisions between like fatty acid molecules to allow some micelles to form with a resultant drop in flotation of mineral.

Tests with Fatty Acids.

120-150 mesh barytes was floated with fatty acids, from n-butyric to stearic, using 0.56 lb. of pine oil per ton of ore. The choice of 0.05 gm. of pine oil per litre gave

FIG - (26)

FLOTATION OF BARYTES
WITH n-BUTYRIC ACID
AS COLLECTOR

FROTHER - 0·56 LB./TON PINE OIL

BARYTES - 120-150 MESH

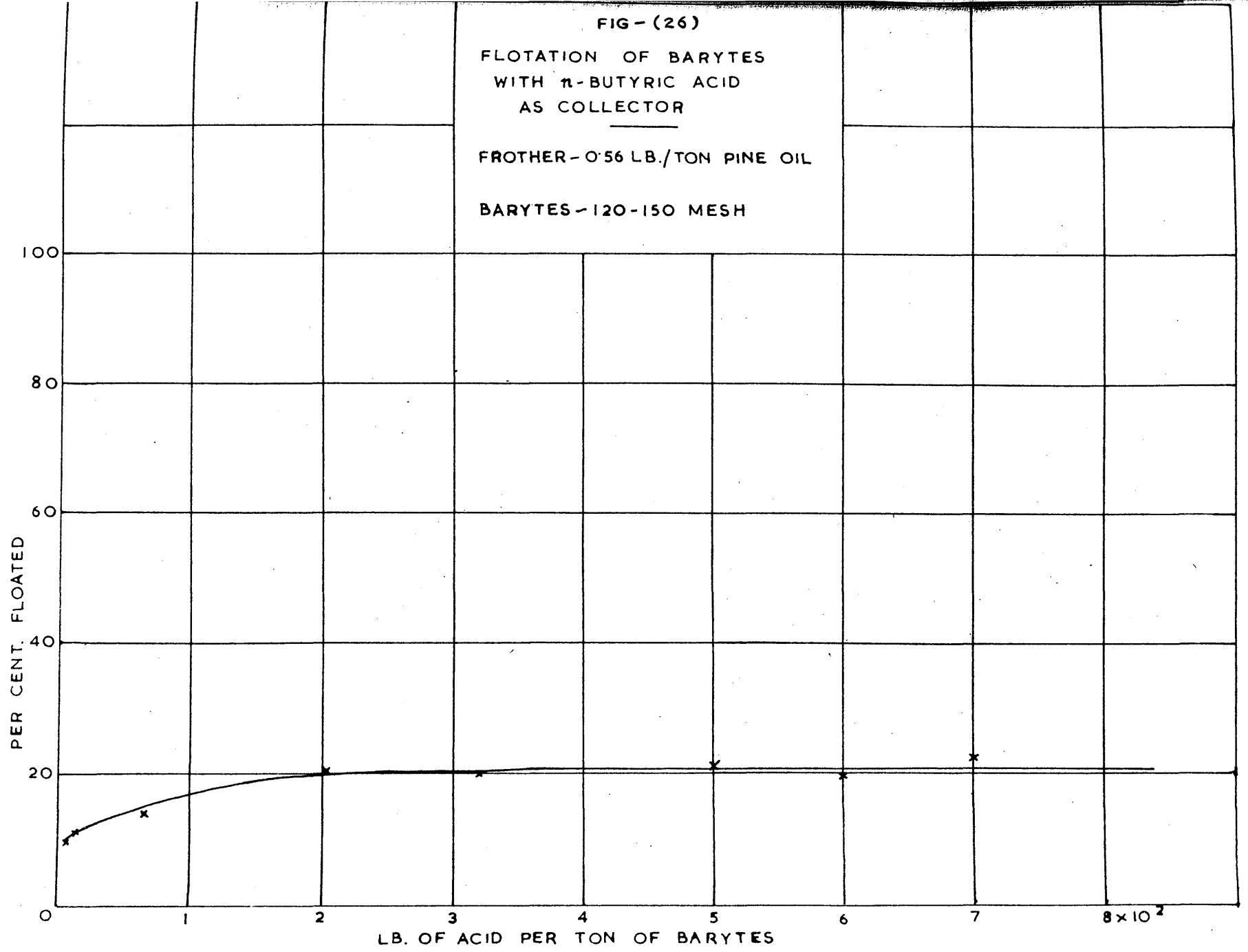


FIG - (27)

FLOTATION OF BARYTES WITH n-VALERIC ACID AS COLLECTOR

FROTHER - 0·56 LB./TON PINE OIL

BARYTES - 120-150 MESH

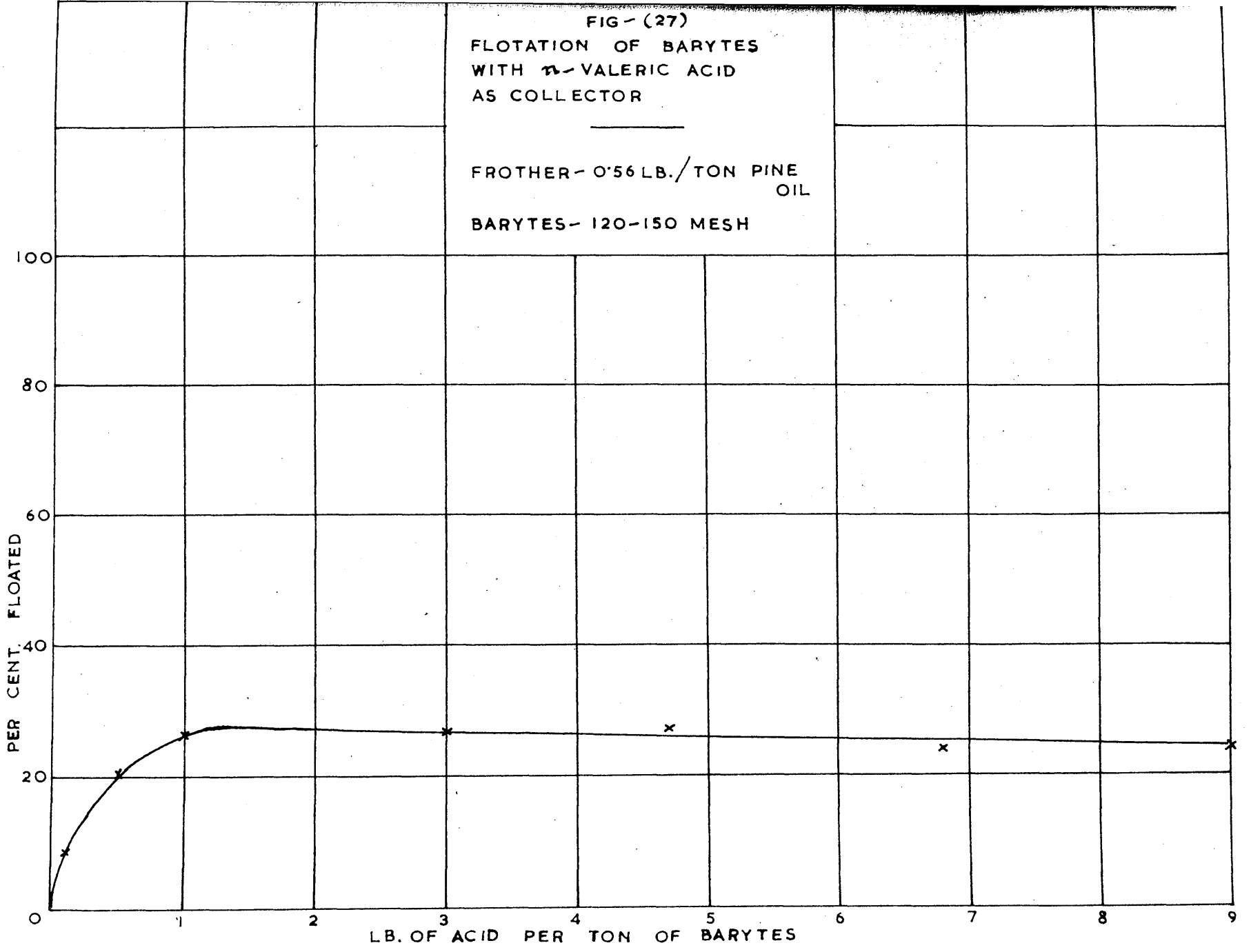


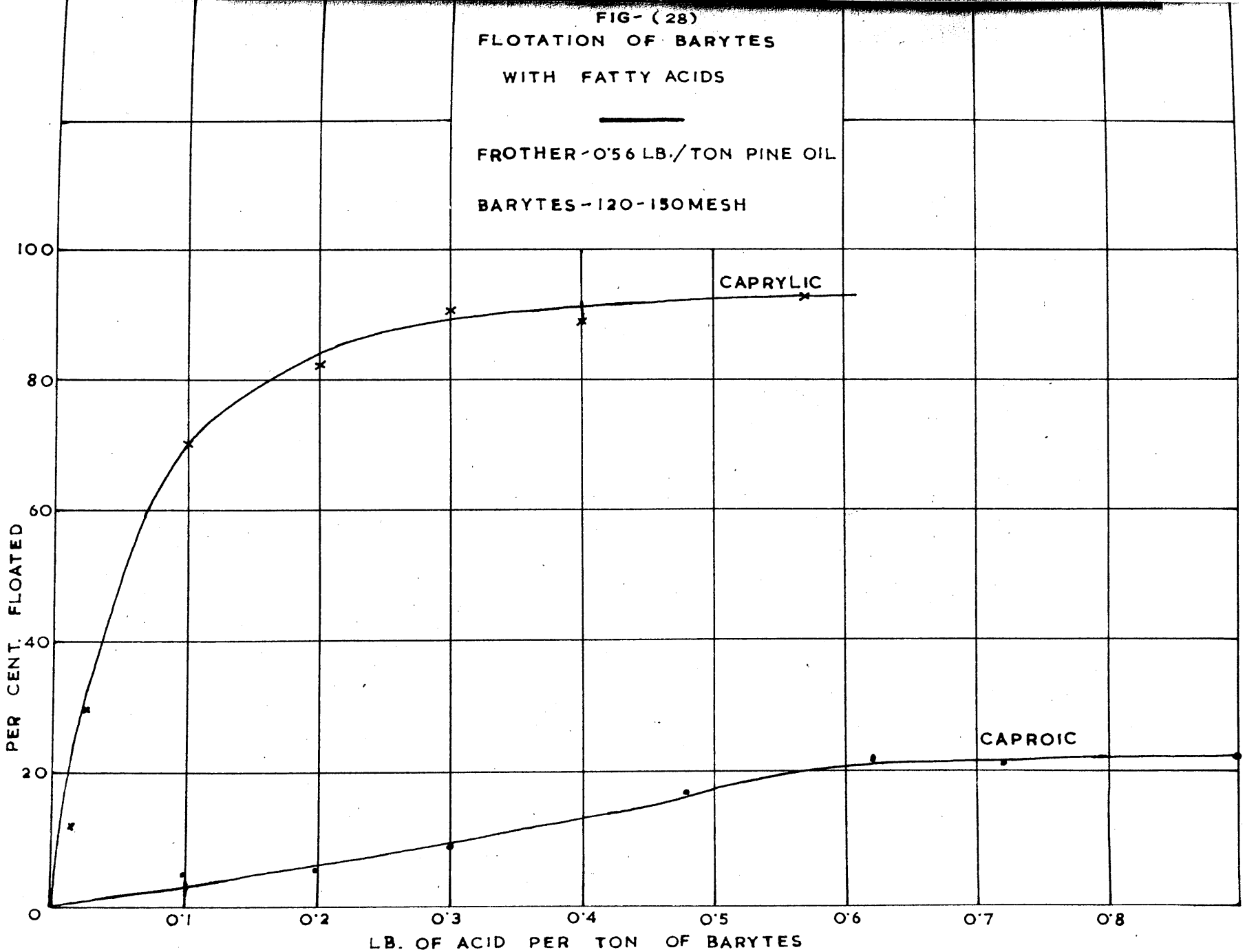
FIG- (28)

FLOTATION OF BARYTES

WITH FATTY ACIDS

FROTHER - 0·56 LB./TON PINE OIL

BARYTES - 120-150 MESH



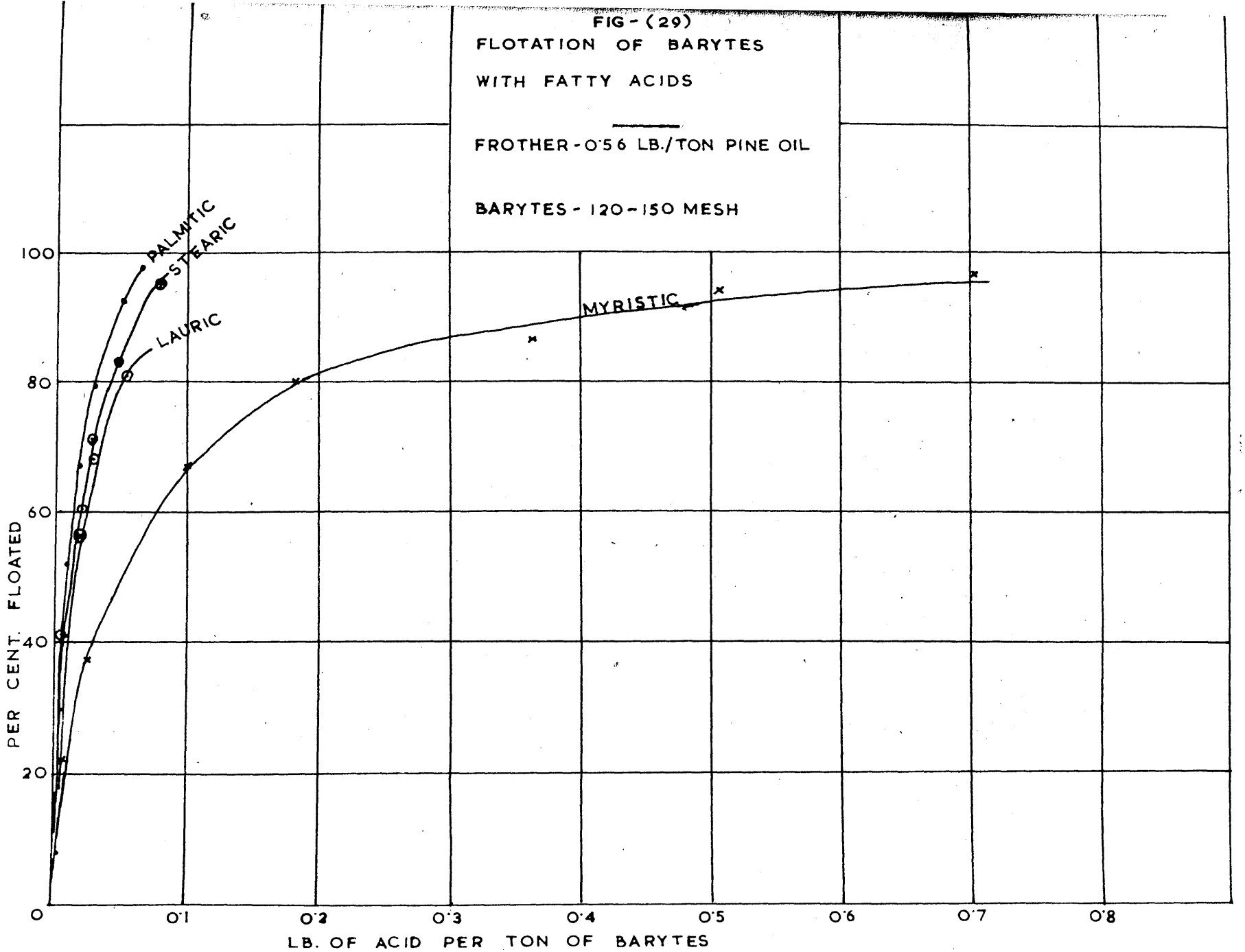


FIG - (29)
FLOTATION OF BARYTES
WITH FATTY ACIDS
FROTHER - 0·56 LB./TON PINE OIL
BARYTES - 120 - 150 MESH
PALMITIC
STEARIC
LAURIC
MYRISTIC
PER CENT. FLOATED
0
20
40
60
80
100
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
LB. OF ACID PER TON OF BARYTES

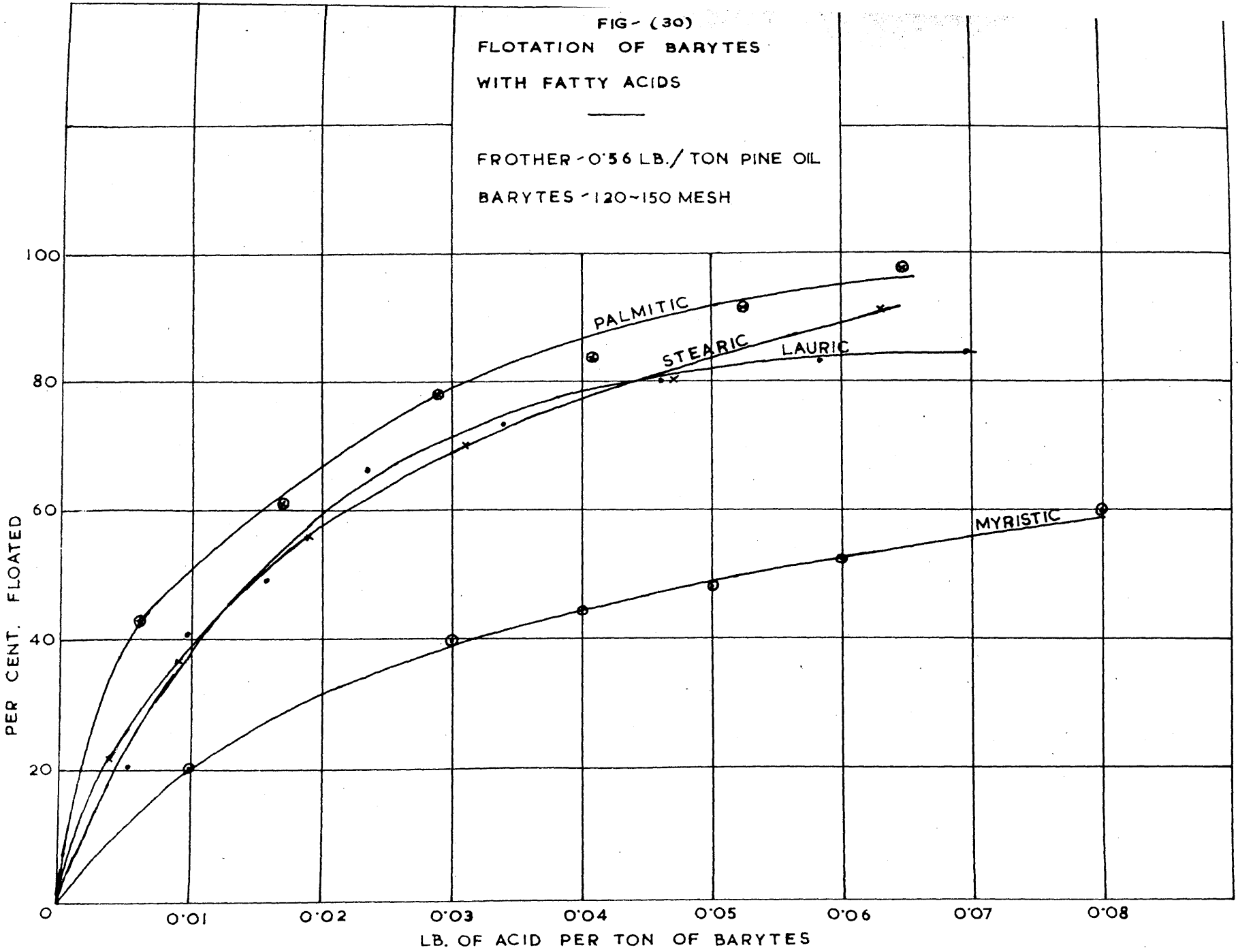


FIG- (30)
FLOTATION OF BARYTES
WITH FATTY ACIDS
FROTHER - 0·56 LB./ TON PINE OIL
BARYTES - 120~150 MESH
PALMITIC
STEARIC
LAURIC
MYRISTIC
PER CENT. FLOATED
LB. OF ACID PER TON OF BARYTES
0
20
40
60
80
100
0·01
0·02
0·03
0·04
0·05
0·06
0·07
0·08

this unusual figure of 0.56 lb./ton. The tests were carried out at the natural pH's of the acid solutions; that is, the pH range of the acid solutions is rather wide, being from about 3 for the concentrated solutions of lower acids to about 6, the pH of distilled water used for making up the solutions, for the higher acids.

The results are given in Figs. (26) to (30). The graphs are drawn separately because of the difference in concentration ranges. Figs. (29) and (30) are the same except that the concentration range of one is ten times that of the other.

In the course of flotation tests with lower acids, the used barytes samples were recovered for further flotation tests by treating with absolute alcohol, ether, alcohol and distilled water in that order. The washing with each liquid was done three times except in the case of distilled water where more than ten to fifteen times was adopted to ensure that no alcohol was left in the solid. That this process removes the collector coating on the mineral particles was demonstrated by an experiment with the Hallimond tube which is described on p.66, Chapter (V). A sample of 130-300 mesh barytes that gave 90 per cent recovery with 0.06 lb./ton lauric acid was shaken twice with 20 cc. of absolute alcohol in a clean test tube followed by several washings with distilled water. It was then floated with merely distilled water in the Hallimond tube. A recovery of only 3.5 per cent was obtained over a period of five minutes. Similar results

was obtained with the coating formed from barytes and 0.1 lb./ton sodium laurate that gave 100 per cent recovery. In fact, washing with absolute alcohol alone in the cold is sufficient to remove the fatty acid or soap coating on barytes.

An interesting result was obtained with a test utilising a large quantity of reagent. 1 cc. of lauric acid solution in methyl alcohol, containing 6.69 gm. per litre, was added to 75 cc. of pine oil solution (0.56 lb./ton) in the cell, making up the concentration to 1 lb. of acid per ton of ore. The frother power of the solution was so appreciably lowered that no overflow occurred at the air-flow rate at which the pine oil solution alone flowed over into the outer cup. Increase of air-flow did not help to produce more froth but large air bubbles. However, when less than 0.2 cc. of the alcoholic solution was added, i.e., when the concentration of acid in the cell is below 0.2 lb./ton or 0.000134 gm./l., the frothing power was enhanced. The only visible change in the resulting solution was that of the precipitation of insoluble lauric acid in a very fine state in the first instance. The fact that methyl alcohol, when added alone in quantities up to 5 cc., had no effect on the frothing power shows that this phenomenon was due to the insoluble acid.

Hardy (55) had shown that on increasing the concentration of oleic acid in water, the stability of the air bubble increased to a maximum on the formation of an unimolecular film and then decreased to nothing on the formation of an oleic acid layer of 10 millimicrons thickness.

Similar results were obtained by Talmud and Suchowolskaja (56) on working with stearic and palmitic acids. These findings are also in line with the results of Gibb on the alcohols and the frothing results for the lower fatty acids given in the earlier part of this work, viz., that a saturated solution or supersaturated solution of a surface active agent has little frothing power. It appears that lauric acid is adsorbed in preference to pine oil at the air-water interface and, these high concentrations, destroys the stability of the froth.

Tests with Soaps.

130-300 mesh barytes was used for flotation with soaps. The concentration of terpineol was 0.5 lb. per ton of mineral. The solutions were maintained at pH 10.4 which is the natural pH of soap solutions. The successive dilution method was employed for preparation of different concentrations.

The results are shown in Fig. (31) and (32). Here also the concentration ranges of the higher and lower acids are different.

Discussion of Results.

The collecting power of the fatty acids increases with the number of carbon atoms in the molecule up to C_{16} or palmitic acid, and it then decreases. Below 0.044 lb./ton concentration, the collecting action of stearic acid is almost the same as that of lauric acid.

In the case of soaps, the collecting power increases with the number of carbon atoms up to C_{14} or sodium myristate

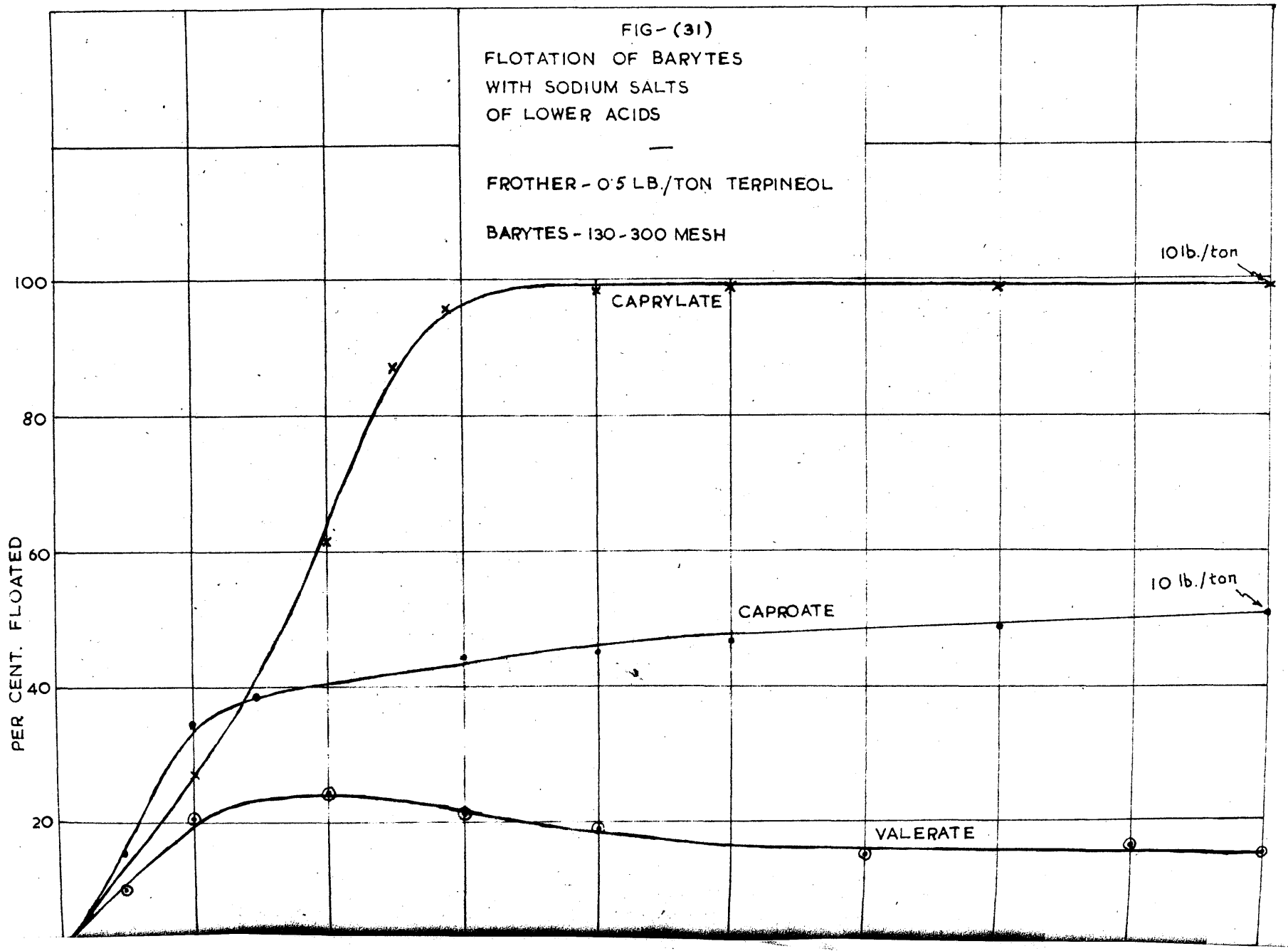
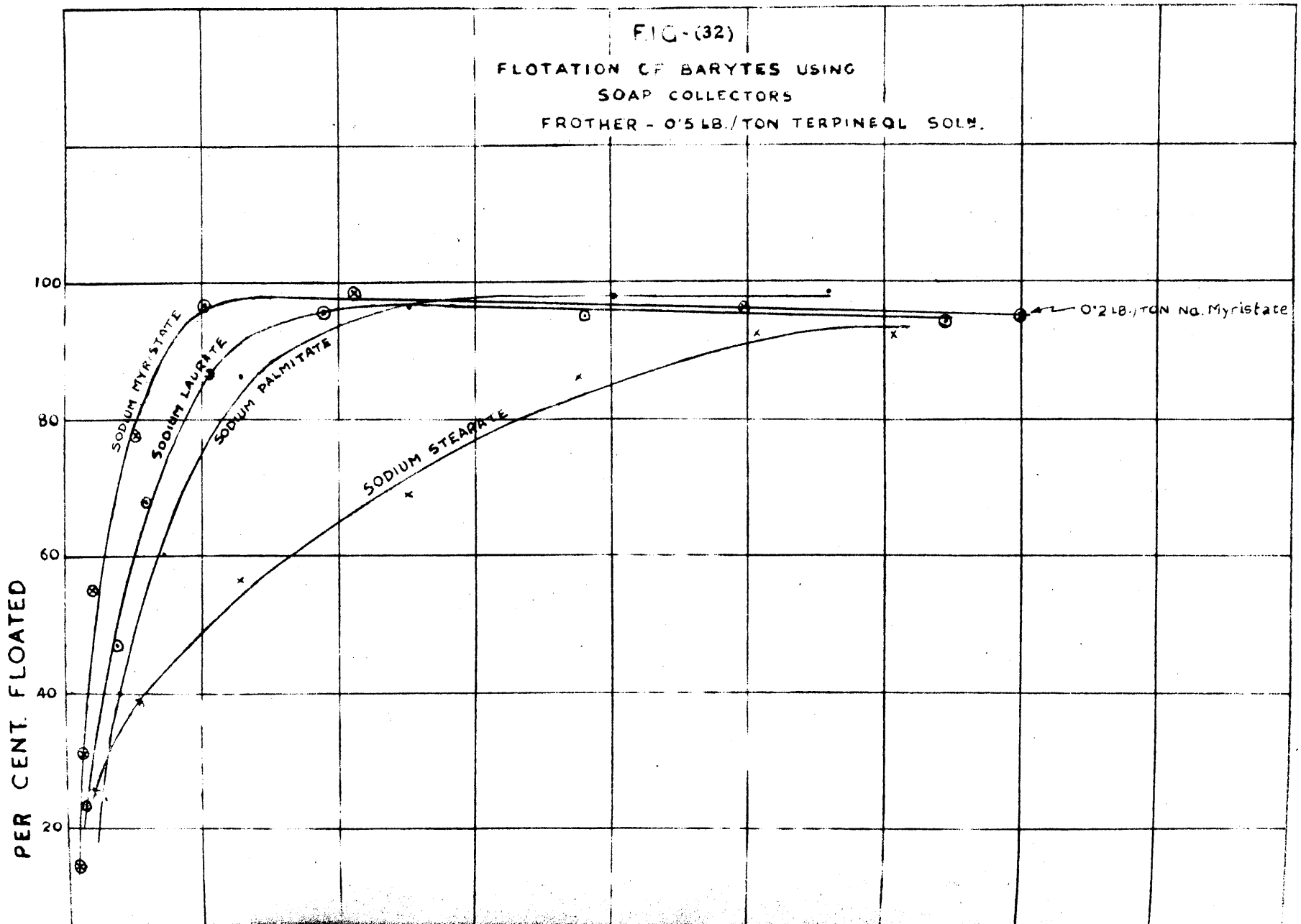


FIG-(31)
FLOTATION OF BARYTES
WITH SODIUM SALTS
OF LOWER ACIDS
FROTHER - 0·5 LB./TON TERPINEOL
BARYTES - 130-300 MESH
PER CENT. FLOATED
100
80
60
40
20
CAPRYLATE
10 lb./ton
CAPROATE
10 lb./ton
VALERATE

FIG-(32)

FLOTATION OF BARYTES USING SOAP COLLECTORS

FROTHER - 0·5 LB./TON TERPINEOL SOLN.



and it then decreases.

A similar observation was made by Keck and his colleagues (53) on floating specular haematite with fatty acids. They found that the flotation increased with the number of carbon atoms until a maximum of 12 carbon atoms was reached; thereafter, flotation apparently decreased with further increase in the number of carbon atoms. It seems, therefore, that there is a critical length of hydrocarbon chain at which the collecting power reaches a maximum for a homologous series. The reason for this is as yet uncertain. It may be that the adsorption is also at a maximum at that critical chain length, or alternatively the surface energy associated with the hydrocarbon group may be at a minimum for this length of chain.

As the percentage of barytes floated with lower acids and their sodium soaps up to C_6 is very low even at high concentrations, they may be regarded as very poor collectors.

A comparison of Figs. (30) and (32) shows that the soaps of the higher fatty acids are better collectors than their corresponding acids, since with all these soaps except sodium stearate a maximum recovery of over 90 per cent. is obtainable at a relatively low concentration of about 0.04 lb./ton. This difference is much greater than the effect of the different size fractions of barytes employed in the two sets of tests. This is only the state of affairs at room temperature. Results may be different at higher

temperatures, e.g., at 60°C. We are, however, primarily interested in room temperature conditions at which flotation is normally carried out.

The only anomaly among the acids is the case of myristic acid whose flotation results are much lower than those of lauric acid, lower in the series.

Adsorption and Collector Requirement.

On the assumption that the whole of the collector is adsorbed on the surface of the mineral floated, the area available per collector ion is calculated for each reagent as given in Table (8) and specimen calculation. The mean surface area of 120-150 mesh barytes determined by Rigden's method is 794.5 $cm^2/gm.$ and that of 130-300 mesh barytes as determined by Lea and Nurse method is 542 $cm^2/gm.$ as stated in the chapter on surface area measurements. On coverting these to the gas adsorption values by multiplying with the factors 1.2 and 1.9, 952.8 and 1029.8 $cm^2/gm.$ respectively were obtained.

Where constant maximum recovery is exhibited, as with all the higher soaps except sodium stearate, the concentration chosen is the least required for maximum recovery obtained by extrapolating the top flat portion of the curve towards the recovery axis and taking the concentration at which this line meets the ascending curve. In other instances, a convenient point near the maximum recovery is chosen. From the percentages of recovery corresponding to these concentrations of collector, the quantities of ore

floated are obtained knowing the total weight of dry ore in each test to be 15 gms.

Specimen Calculation for Area Available per Collector Ion Sodium Myristate.

Maximum recovery at 0.03 lb./ton concentration.

Since 1 lb./ton $\doteq$ 0.0894 gm./l. solution concentration,

0.03 .. .. $\doteq$ 0.0894 x 0.03 gm./l.

i.e., total quantity of collector in 75 cc. test solution

$$= \frac{0.0894 \times 0.03 \times 75}{1000} \text{ gms.}$$

$$\text{or} = \frac{0.0894 \times 0.03 \times 75}{1000 \times 250} \text{ gm. mols.}$$

i.e., for 15 x 0.97 gms. of floated mineral there are

$$\frac{0.084 \times 0.03 \times 75 \times 6.02 \times 10^{23}}{1000 \times 250} \text{ molecules}$$

or, 1 gm. ..... $\frac{0.0894 \times 0.03 \times 75 \times 6.02 \times 10^{23}}{1000 \times 250 \times 15 \times 0.97}$ mols.

$$= y \text{ mols. (say).}$$

Specific Surface of barytes = 1029.8 cm^2./gm.(Lea and Nurse)

Therefore, area available per molecule

$$= \left(\frac{1029.8 \times 15 \times 100x}{0.0894 \times 75 \times 6.02 \times 10^{23}}\right) \times \frac{250 \times 0.97}{0.03} \text{ cm}^2$$

$$= (3.27 \times 10^{-18}) \times \frac{250 \times 0.97}{0.03} = 309.4 \times 10^{-16} \text{ cm}^2$$

or, 309.4 Å^2

Number of Collector Ions per Unit Cell Area.

In Table (8) the second last column represents the number of molecules per 'unit cell area'. By the latter is meant the average area of the three surfaces of unit cell bounded by the axes, a, b, and c. X-ray analysis of barytes was first done by James and Wood (57). According to them, a projection of the unit cell upon 010 face is as drawn in Fig. (33). In this figure, the atoms of barium, sulphur, and oxygen, are drawn approximately in proportion to their actual ionic radii, which are 1.43 Å, 0.34 Å, and 1.32 Å respectively. The numbers represent the distances of the atoms from the 010 face. Dividing the 'b' axis (vertical to the 010 face and out of the plane of the diagram) into 100 parts, the number 75 will thus be $\frac{3}{4}$ th. of the 'b' axis, taking the plane of the paper as the datum plane. Each Barium atom lies between 12 oxygen atoms belonging to seven different sulphate groups. The lattice type is orthorhombic and the dimensions of the three axes are:-

$$a:b:c = 8.85\ \text{Å} : 5.44\ \text{Å} : 7.13\ \text{Å}.$$

The average of the three areas formed by these three axes, i.e., axb, bxc, cxa, is obtained as 50.1 Å^2 and this is taken as probable unit cell area. With the same assumptions as in the previous calculation, the number of collector ions in one unit cell area is calculated as shown below.

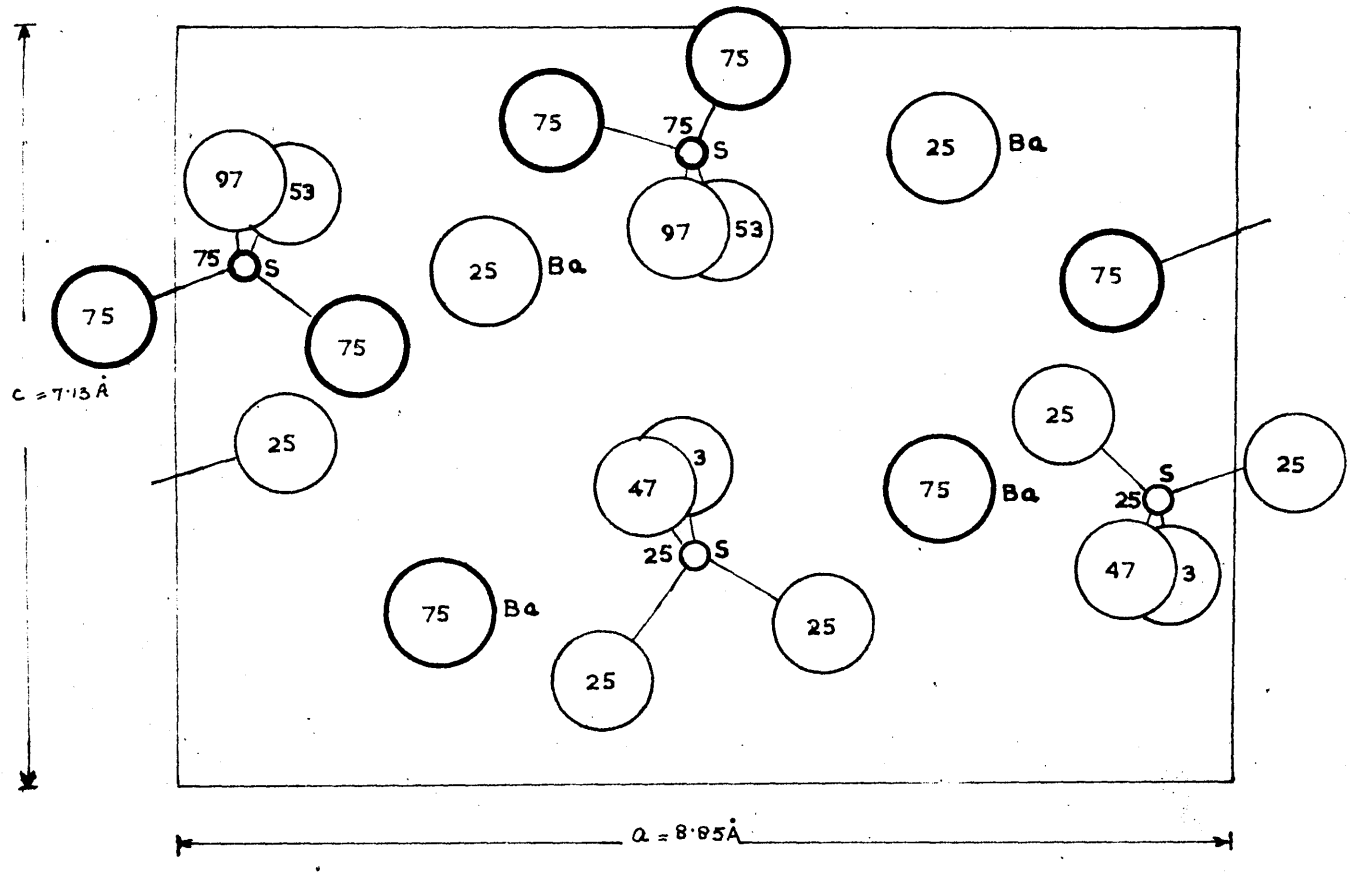
Specimen Calculation.

Sodium Myristate.

From the foregoing calculation, the number of

FIG-(33)

THE UNIT CELL OF BARYTES
PROJECTED UPON THE (010) FACE



molecules per gm. or 1029.8 $cm.^2$ of surface is (y). Hence for 50.1×10^{-16} $cm.^2$ surface there are:-

$$\frac{y \times 50.1 \times 10^{-16}}{1029.8} \quad \text{molecules}$$

$$= \left(\frac{0.0894 \times 75 \times 6.02 \times 10^{23} \times 50 \times 10^{-16}}{1000 \times 15 \times 1029.8}\right) \times \frac{0.03}{250 \times 0.97}$$

$$= (1.309 \times 10^{2}) \times \frac{0.03}{250 \times 0.97}$$

$$= 0.016 \text{ molecule.}$$

N.B. In the above calculations, the constant quantities in brackets are turned into factors to reduce mathematical work.

The results of similar calculations for mill concentrates, obtained by Gaudin and Preller (58), are shown in Table (9). Their calculations were based on the following assumptions:-

(1) That all the collecting agent is utilised; i.e., the residual collector concentration in the liquor is negligible.

(2) That no collector is wasted either by evaporation or by formation of insoluble precipitates.

(3) That the otherwise collectible mineral actually collected has not consumed any collector.

(4) That the concentrate surface as measured is entirely due to the collected minerals, and not diluents of small weight but large surface, such as clay minerals.

(5) That the surface accessible to nitrogen in the gas

adsorption method is the same as the surface accessible to the collector ions.

Giving reasons for and against the justification in making the above assumptions, they suggest that all subsequent work be carried out in laboratory since, by so doing, the necessary conditions can be selected in order that the assumptions become true.

The results in Table (8) show that the area available per ion is, in all cases except those of caprylic acid and sodium caprylate, greater than the "parking area" of the fatty acid or soap molecule. It may, therefore, be concluded that maximum recovery may be attained without the formation of a close-packed mono-ionic layer of the collector. This conclusion is supported by the figures of Gaudin and Preller in Table (9). There seems to be no relationship between the two areas. Taking the cross-section of a fatty acid molecule as 20.5 Å2, it can be seen that the area available per ion varies from about two to fifteen times the cross-sectional area. In terms of 'unit areas' this amounts to about 17 to 80 ions per 1000 'unit areas'.

Gaudin and Prellers' assumption No. 1 above, which is the same as the author's assumption on which the calculations were based, is not strictly true. Actual quantities adsorbed will be lower than the values taken as there must be equilibrium concentration of the collector in solution. Hence the area available per ion will still be larger than the estimated value in every case in the tables given. Possibly with

n-caprylic acid and its sodium salt monolayers have been formed at maximum recovery.

Contrary to the results obtained here Held and Samochwalov (19) found from a study of the adsorption of sodium laurate by barium sulphate that the mineral floats best when completely coated with a monomolecular film of the collector.

The reciprocal of "molecules per unit area" gives the 'unit areas' occupied by a collector ion. The approximate number of 'unit areas' per ion for each collector is shown in the last column in Table (8). With the exception of sodium caprylate and caprylic acid, the collector ion occupies a fairly large area composed of from about 20 to 60 'unit areas'. Now Fig. (33) shows the presence of only two barium atoms on each of the two planes, viz. (25) and (75), parallel to the projected 010 face; i.e., there are two barium atoms per unit area. In other words, only one collector ion is adsorbed to every 40 to 120 barium atoms, a ratio which is much greater than the stoichiometric ratio of two collector ions to one barium atom required by reaction hypothesis. Gaudin and Preller also found that one xanthate ion is adsorbed to every two lead atoms on the galena surface instead of in the proportion required for lead xanthate formation which is two of xanthate to one of lead. This suggests that it is simply a case of physical adsorption and not chemical reaction between the mineral and collector.

Effect of pH.

The pH value is well recognised as a very important

Table (9).

Mill Concentrated.	Collector	Specific Surface of Ore. $m^2/gm.$	Area Available Per/Ion = $A^{\cdot 2}$	Area Coverable by collecting ions on close packed Basis = $A^{\cdot 2}$
Morenci conc.	Na dipropyl dithiophosphate	0.98	96.4	45
Pyrite, Galena	Ketxanthate	1.87, 0.43	64.2	29
Anaconda Copper Co.	Na Etxanthate	1.5	237.6	29
Utah Copper Co.	Na dicresyl dithiophosphate	1.4	182	53
Sullivan Galena	Kisopropyl xanthate	0.64	32.5	29

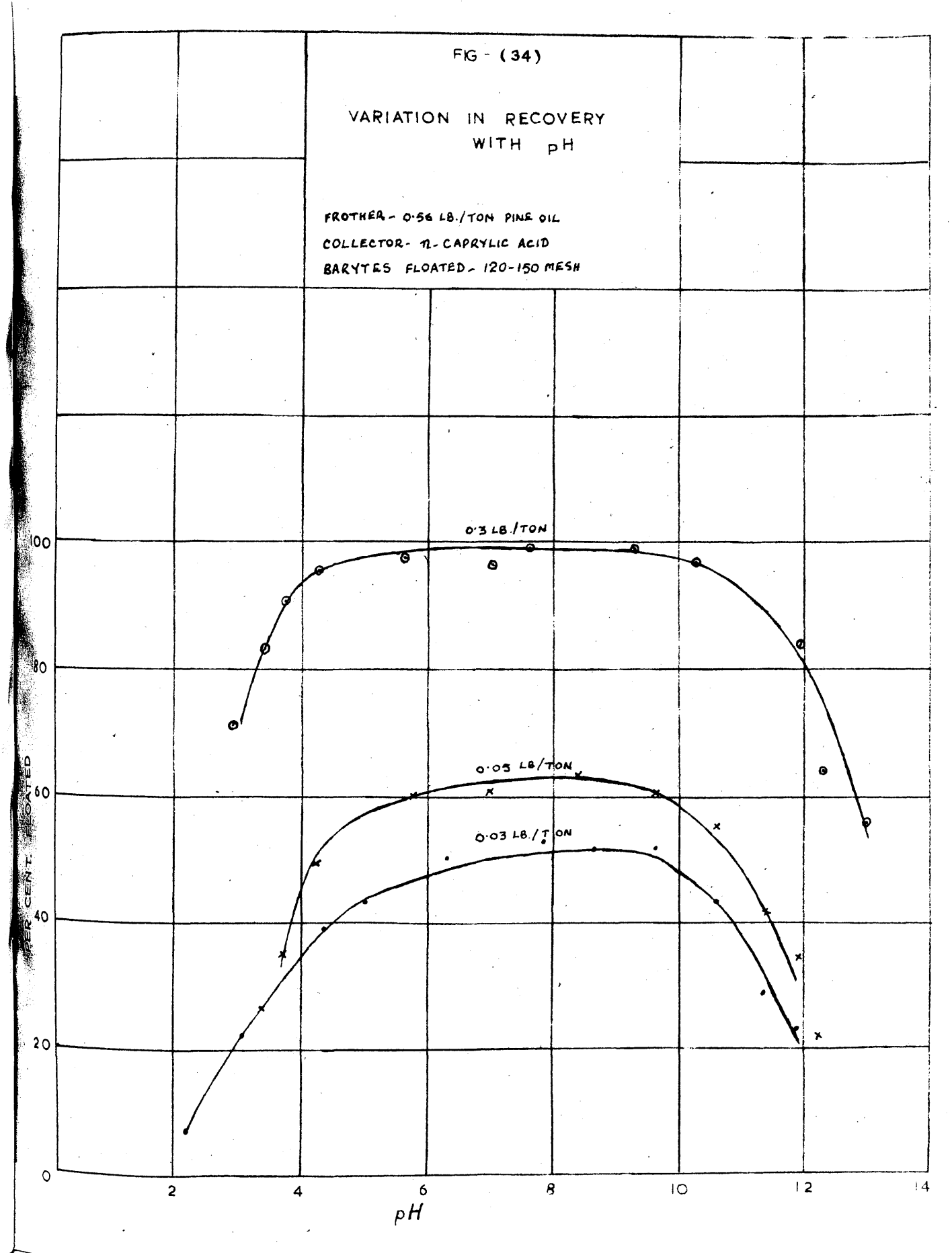
TABLE (8).

Collector	Least Concⁿ for maximum recovery. lb./ton.	Maximum Recovery Per Cent.	Specific Surface of ore. $cm.^2/gm.$	Cross-Section of Molecule A^2	Area Available Per Ion A^2	No. of Mols. Per Unit Cell Area.	No. of Unit Cell Areas Per Ion.
n.caprylic acid	0.47	93	1033	20.5	10.91	0.46	2.2
lauric acid	0.064	85	"	"	101.6	0.049	20.
myristic acid	0.08	58	"	"	63.2	0.080	13.
palmitic acid	0.06	94	"	"	151.1	0.034	30.
stearic acid	0.06	87	"	"	40.0	0.033	30.
sodium caprylate	3.7	98	1029.8	"	1.72	6.76	0.15
sodium laurate	0.045	96	"	"	181.3	0.028	33
sodium myristate	0.030	97	"	"	309.4	0.017	60
sodium palmitate	0.062	98	"	"	168.2	0.030	33
sodium stearate	0.12	92	"	"	88.4	0.057	18

FIG - (34)

VARIATION IN RECOVERY WITH pH

FROTHER - 0·56 LB./TON PINE OIL
COLLECTOR - n-CAPRYLIC ACID
BARYTES FLOATED - 120-150 MESH



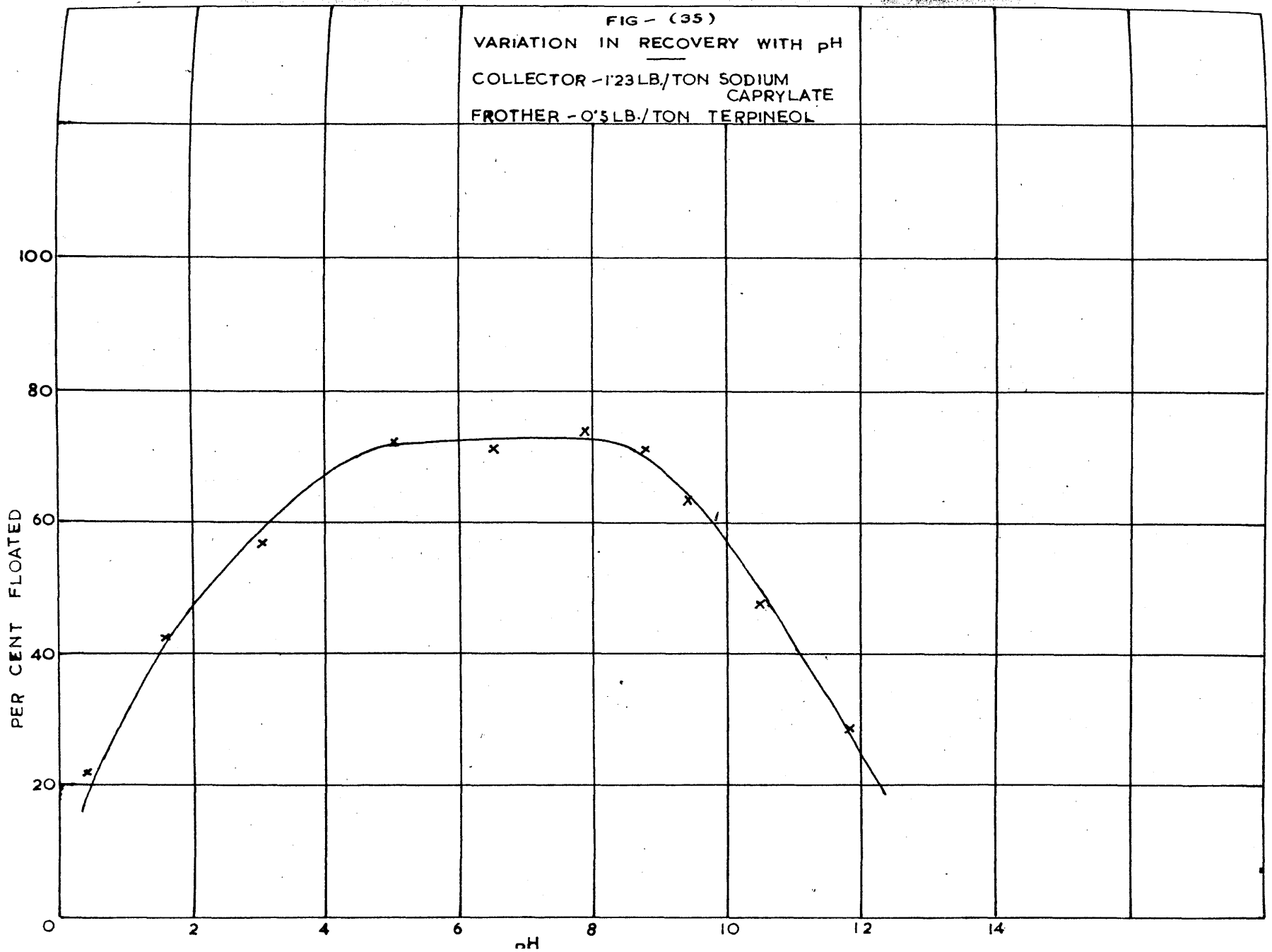
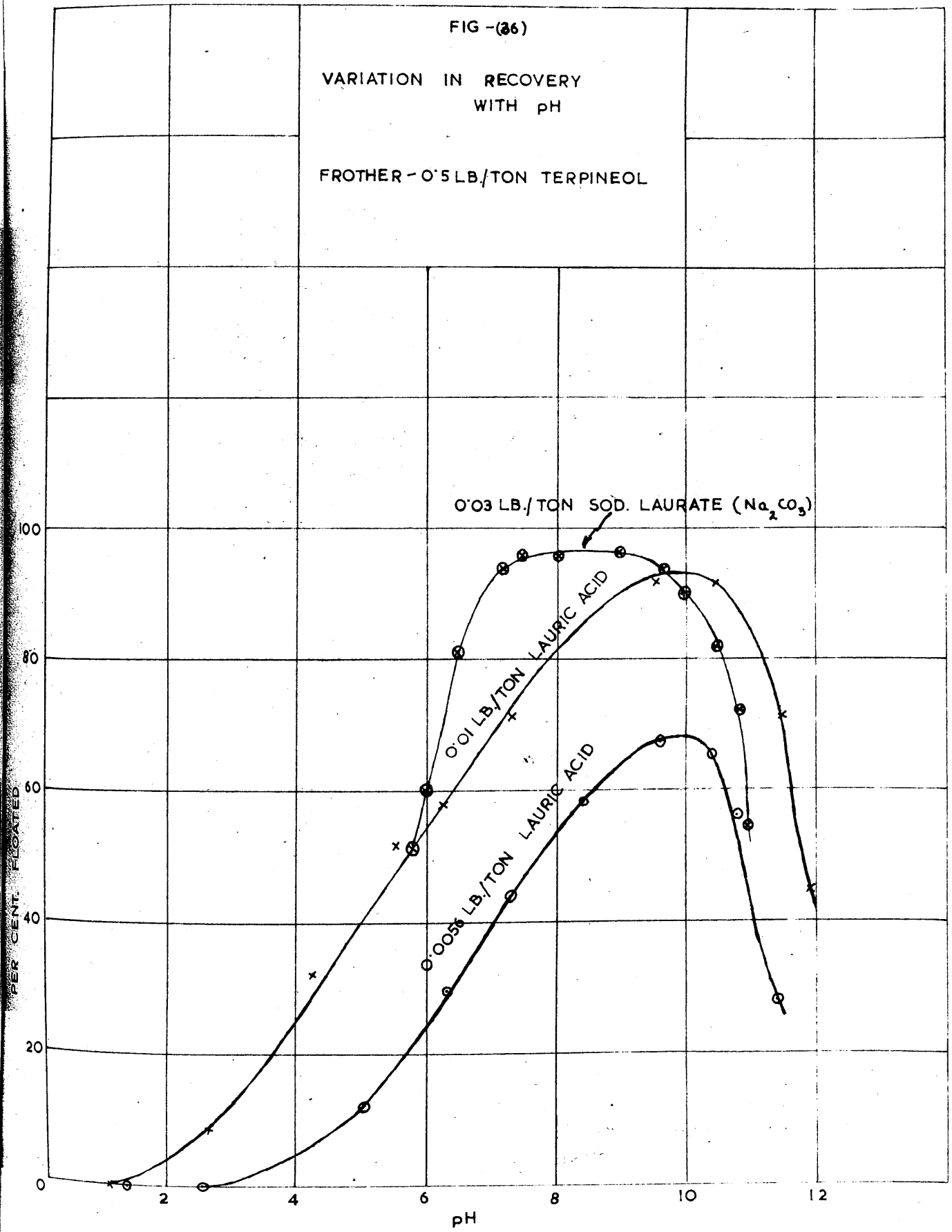


FIG - (35)
VARIATION IN RECOVERY WITH pH
COLLECTOR - 1·23 LB./TON SODIUM CAPRYLATE
FROTHER - 0·5 LB./TON TERPINEOL
PER CENT FLOATED
100
80
60
40
20
0
2
4
6
8
10
12
14
pH

FIG -(36)

VARIATION IN RECOVERY WITH pH

FROTHER - 0·5 LB./TON TERPINEOL



factor in flotation especially with fatty acids and soaps. To find out its effect on flotation of barytes it was decided to use first n-caprylic acid not only because of its being an intermediate member of the series but also because of its relatively high collecting power. From among the higher members lauric acid was chosen owing to the fact that its solubility in water is higher than that of the other three acids and it is most easily prepared by recrystallisation from alcohol solution.

Sulphuric acid and caustic soda were used to vary the pH on acid and alkaline sides respectively. The results for the three different concentrations of n-caprylic acid are given in Fig. (34). Neutralising this acid first with caustic soda to obtain sodium caprylate and then varying the pH of the solutions gave similar results as shown in Fig.(35). The effect of pH on flotation with lauric acid is illustrated in Fig. (36).

The following deductions can be drawn from the results:-

1) ... Taking n-caprylic acid as typical of the intermediate members possessing properties in between the higher and lower members, it can be said that, for fatty acids having moderately high collecting power, there exists a pH range within which a nearly constant maximum recovery is attained. On either side of this range the recovery decreases with acidity or alkalinity.

2) ... From the low recoveries obtained with n-valeric, acid,

n-caproic acid and their sodium salts, it may be presumed that pH variation will have very little effect on flotation with these acids. We may, therefore, expect the pH range for maximum recovery to become narrower as the homologous series is ascended.

3) ... The effect of pH becomes more pronounced as the collecting power of the acid increases. Thus the flat maximum in the pH vs. recovery curve disappears with lauric acid as was expected. The best recovery with both concentrations of lauric acid were obtained at pH 10 which is almost identical with the natural pH of soap solutions (pH = 10.4).

4) ... With caprylic acid the constant maximum recovery lies between pH 6 and pH 9. As the concentration of the acid is decreased, it seems that the flat maximum in the curve is reduced in width and becomes less pronounced. This indicates that for acid solutions possessing high collecting power the addition of acid or alkali has little influence on flotation over a wide pH range. Apparently, this does not apply in the case of higher acids such as lauric acid where no constant recovery with pH is obtainable. The explanation may lie in different degrees of dissociation of the lower and higher acids. Caprylic acid being stronger than lauric acid it seems to be dissociated sufficiently at a pH of about 6 (where constant recovery starts) to provide the necessary number of ions for maximum flotation. On the other hand, the dissociation of lauric acid appears to reach the maximum only at pH 10. Indirectly, therefore, these results are supporting

the theory of Wark and Cox, already mentioned, that the ions, caprylate and laurate ions here, and not the neutral molecules of Cook and Nixon, are responsible for the collecting action.

5) ... 1.23 lb./ton concentration of sodium caprylate corresponds to 1.07 lb./ton caprylic acid solution. The concentration in terms of caprylic acid being higher than the highest concentration of caprylic acid (0.3 lb./ton) tested in Fig. (34), a higher maximum recovery would naturally be expected. From a comparison of Figs. (34) and (35), it can be seen that the reverse is the case. This may have been due to the use of a new flotation cell with apparently larger pore size. The experiments with caprylic acid were conducted by using the first cell having smaller pores in the sintered glass diaphragm. A detail statement on this phenomenon has been made in the section of flotation cells on p.(56).
The similarity in the results for sodium caprylate and caprylic acid, however, indicates that the same effect can be achieved either by taking the acid or its sodium soap.

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EFFECT OF ANIONS AND CATIONS ON FLOTATION OF BARYTES WITH SODIUM LAURATE.

Chapter VIII.

Activation and Depression.

It is known that inorganic salts, added to a flotation circuit, can bring about either an activation or a depression of the flotation of minerals. The most extensively used activation process is the treatment of sphalerite with copper sulphate. Although general agreement has been reached that the activation is due to a reaction between the mineral and the copper salt with the result that copper sulphide is formed on the surface, as stated earlier, the actual mechanism of activation is still undecided.

Taggart, Gaudin and others supposed that the surface of sphalerite is turned into covellite structure by double decomposition, while Wark and Wark (59) contended that a monomolecular film of cupric sulphide is formed on the surface by replacement of zinc ions of the lattice by copper ions. The latter authors pointed out the difference in the two copper sulphide coatings and the valency forces available at the surface by a consideration of the disposition of ions forming the film as in the diagrams below.

Cu	S	Cu	S	Cu		Cu	S	Cu	S	Cu	S
S	Cu	S	Cu	S		S	Zn	S	Zn	S	Zn
Cu	S	Cu	S	Cu		Zn	S	Zn	S	Zn	S
Massive Covellite						Film of CuS on Sphalerite					

In support of Wark and Wark, Ravitz and Wall (60) found from the relation between the concentration of copper sulphate and the amount of copper abstracted from solution by sphalerite particles of various sizes, that a monomolecular film of copper sulphide completely prevents further penetration of copper ions into the sphalerite crystal.

Apart from sphalerite activation by copper sulphate, it is not known definitely whether a reaction between the activator and the mineral is a necessary step to activation. It would certainly be difficult to say that such a reaction has taken place in a case like the activation of silica by iron or by barium salts in presence of soap collectors. Nevertheless, whatever be the mechanism, as a general rule the ions that are effective as activators form relatively insoluble salts with the ions of opposite charge from the crystal lattic of the mineral. Solubility, however, may not be the only governing factor.

As to the depressants, there are two types; those which prevent the collector from functioning by changing the mineral surface in some way, and those which reduce the collector concentration in solution by forming an insoluble precipitate with the collector. Here again, the interpretation of the mechanism of depression, especially as regards the first type, differs with the school of thought.

Usually the change in the surface of the mineral is attributed to the formation of very insoluble surface coatings by double decomposition. Thus, Gaudin, et al, (7),

regarded the chromate depression of galena as being caused by the formation of an insoluble coating of lead chromate which does not react with ethyl xanthate. As already mentioned, Wark and Cox refuted this hypothesis by showing that lead chromate is floated by ethyl xanthate. In line with their collector theory, the Taggart school are of the opinion that all depressants act via chemical reaction with the mineral surface. The solubility factor seems to be important for the depressants too. Consequently, the Paneth-Horovitz adsorption rule can be made to apply in a number of cases. This rule states that there will be a strong adsorption on an ionic lattice of those ions which form a difficultly soluble or weakly dissociated compound with the oppositely charged ion of the lattice. Examples are the strong adsorption of barium and sulphate ions by barium sulphate and silver and halide ions by the silver halide. In spite of these solubility implications and possibilities of chemical reactions, the recent researches on adsorption of ions in solution by crystals are leading the investigators to look at the activation and depression phenomena in the light of adsorption and not compound formation.

From captive-bubble tests on purified minerals using sodium cetyl sulphate as the collector and various metal salts as the activator or depressant in a controlled pH environment, Rogers and Sutherland (25) enumerated five principles for determining the value of an inorganic reagent as an activator or depressant. They are:-

1) ... All minerals adsorb H^+ and/or OH^- so that the pH of the solution largely determines the adsorptive properties.

2) ... Depressants are compounds which contain an active ion of the same polarity as the collector.

3) ... Activators are compounds containing an active ion of the opposite polarity to that of the collector.

4) ... An ion may act as an activator even though there may be an apparent lack of chemical bonds for linking mineral and collector.

5) ... Pseudo-depressants are usually ions of opposite polarity to that of the collector, which precipitate, and hence reduce, the collector concentration to below the minimum required for flotation.

EXPERIMENTAL.

The effect of various ions on the flotation of barytes with the fatty acids was now studied. First a number of anions were tested and then the influence of the cations.

EFFECT OF ANIONS.

Hydroxyl Ions.

It has been shown previously that with n-caprylic acid and sodium caprylate as collectors, the increase in pH to the alkaline side, at first, did not appreciably alter the maximum recovery but when the solution pH reaches a certain value between 9 and 10, the recovery begins to fall rapidly. With sodium laurate, however, increase in pH beyond 7 at first favoured flotation and then caused a marked depression

after having attained a maximum recovery at pH 10. It is most probable that the total concentration of acid present in solution is the deciding factor for the breadth of the maximum of the pH vs. recovery curve. Irrespective of the degree of hydrolysis of the soap formed on adding sodium hydroxide, the greater the total acid present the greater will be the number of active anions for adsorption on the mineral surface. The breadth of the flat portion of the curve becomes less defined with lower concentrations of caprylic acid and similarly, as shown later, a sharp maximum is changed to a flat one when a higher concentration of 0.03 lb./ton sodium laurate was used with sodium carbonate as given in Fig. (36).

Evidently, the degree of hydrolysis plays an important part in the case of lauric acid judging from the pronounced influence of pH on flotation with this acid revealed by the curves in Fig. (36). Long, Nutting and Harkins (61) and Long and Nutting (62) have worked on the change in surface tension of sodium laurate solution with pH. Their results indicate that in 0.005 M buffered solution, the laurate ion begins to show appreciable hydrolysis to free acid at a solution pH of about 10 and is largely converted to free acid at about pH 7, as far as the surface phase of the solution is concerned. If a similar relationship holds true for the bulk of the solution, the pH at which maximum recovery occurs for lauric acid, i.e., pH 10, probably corresponds to the point of least hydrolysis of sodium laurate.

Owing to the lack of data on the variation with pH of the degree of hydrolysis of sodium laurate, or of the degree of dissociation of lauric acid, it was not possible to determine the concentration of the active laurate ion concentration in solution at any pH.

Most investigators are in agreement with Roger and Sutherlands' (25) conclusion that the variation in flotation with pH is determined by the extent of adsorption of hydroxyl and hydrogen ions. Since in the alkaline solutions, there is a preponderance of hydroxyl ions over the laurate ions, the replacement of the latter by hydroxyl ions after reaching maximum recovery will proceed at a rapid pace. Such an adsorption will naturally make the surface hydrophilic.

A similar explanation, offered by Taggart and Arbiter (63) was based on the report by Soyenkoff (64) and McBain (65) that basic soaps were formed by the addition of hydroxyl ions to soap solutions. They found that with every mineral tested, the contact angle falls with increasing alkalinity of sodium oleate solution and that this occurs in the pH range in which the metallic hydroxides precipitate. Hence they proposed that there is a hydroxyl-oleate contest for the anchored metal ion resulting in progressive displacement of oleate ion as the hydroxyl ion concentration of the surrounding increases. This process is in complete accord with the kinetic concept of equilibrium. To account for the return to the contact angle at optimum pH on transferring the

tested specimen to an aqueous solution having that same pH, they postulated that the displaced oleate ions are held approximately in place by mutual attraction for the yet bound oleate ion of the metal-soap coating, but with the freedom to orient with the carboxyl group end toward the water. Sodium ions of the sodium hydroxide were taken as counter ions for these displaced oleate ions.

Carbonate Ion.

Sodium carbonate was used to determine the effect of carbonate ion on the flotation with sodium laurate. In Fig. (37) is given the change in recovery with concentration of anhydrous sodium carbonate, and pH of tailing water.

From the figure, it can be seen that:-

1) ... An activation of flotation takes place with the initial additions of sodium carbonate owing to increase in pH of the solution.

2) ... The recovery begins to decline after a concentration of about 0.4 lb./ton sodium carbonate. The rate of fall in recovery with concentration is, however, very slow, as about 85 lb. of sodium carbonate needs to be added to a ton of barytes to bring the recovery back to the initial value. This indicates that the OH^- ions and not the carbonate ions are the governing factor in the depressing action for as much an increase in concentration as 56 lb./ton sodium carbonate is required to change the pH from about 10 to 10.8. It should be noted that a reversible reaction between sodium carbonate and barium sulphate is possible:-

$$CO_3^{--} + BaSO_4 = BaCO_3 + SO_4^{--}$$

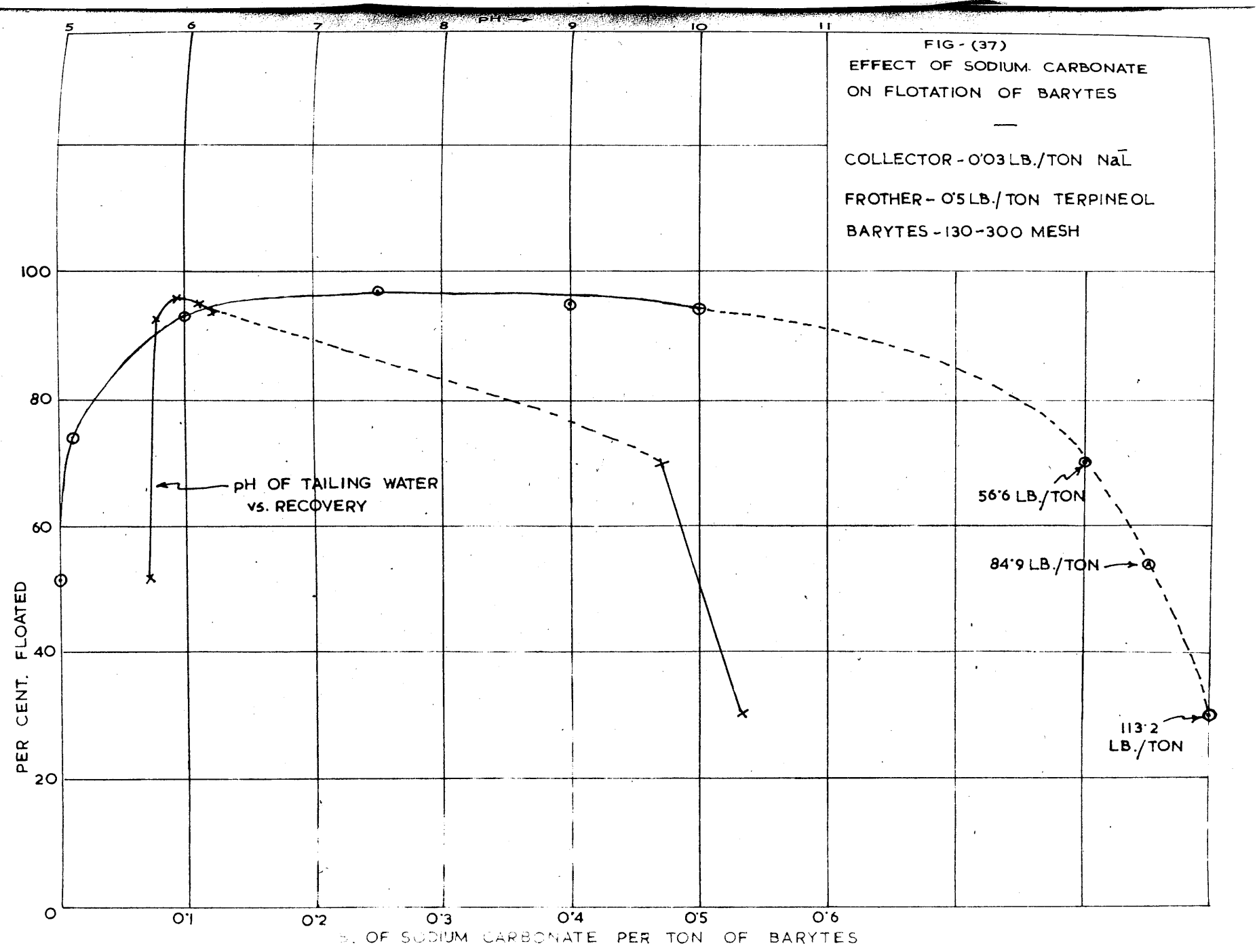


FIG - (37)
EFFECT OF SODIUM CARBONATE ON FLOTATION OF BARYTES
COLLECTOR - 0·03 LB./TON NaĀL
FROTHER - 0·5 LB./TON TERPINEOL
BARYTES - 130-300 MESH
pH →
5
6
7
8
9
10
11
100
80
60
40
20
0
PER CENT. FLOATED
pH OF TAILING WATER vs. RECOVERY
56·6 LB./TON
84·9 LB./TON
113·2 LB./TON
0·1
0·2
0·3
0·4
0·5
0·6
% OF SODIUM CARBONATE PER TON OF BARYTES

Apparently, this reaction has no effect on the flotation with sodium laurate.

3) ... The pH vs. recovery curve in Fig. (36) is of a similar type as that obtained with lauric acid and caustic soda. The difference between this and the curves for lauric acid is that the maximum recovery remains almost constant in the pH range 7.5 to 9. The probable reason for this has been given above. The steep drop in recovery with pH on the alkaline side is probably due to the depression caused by the large excess concentration of sodium carbonate in addition to that of the OH^- ions. It is well known that a large amount of any inorganic salt is capable of depressing any mineral, i.e., of imparting salt effect. The frothing property of the solution will be affected as well.

4) ... The pH of the tailing water remains nearly constant at about pH 6, even though the recovery has risen considerably, and the pH of the original solution has increased to 10. It then increases with increase in recovery. The explanation for this constancy in pH is the relatively high increase in frothing power of the solution as the concentration of sodium carbonate becomes greater and hydrolysis of sodium laurate consequently reduced. The final result is that the tailing water is chiefly composed of the frother solution introduced during flotation. As the recovery decreases after reaching the maximum, the frothing power also declines but the high pH of the tailing water really should be attributed to the use of a large excess of sodium carbonate in the original solution.

Sulphate Ion.

As sulphate ion is the common ion of the crystal lattice of barytes, its effect on flotation with sodium laurate was investigated by flotation tests with different quantities of sodium sulphate dissolved in the frother-collector solution. The results, obtained at a constant pH of 5.92, are shown in Fig. (38), and they indicate a decrease in recovery with increasing sodium sulphate concentration. This decrease becomes constant for concentrations higher than 0,08 lb./ton. The depression of barytes by sulphate ions was also noticed by Held and Dyachkov (66) using, nonylic acid as collector.

Having the same polarity as the collector laurate ion, the sulphate depression was thought to be due to the adsorption of sulphate ions on the barytes surface in place of laurate ions, as according to Rogers and Sutherlands' Principle (2) above. If 0.08 lb./ton of sodium sulphate from Fig.(38) were taken as the concentration at which the adsorption of sulphate ion is almost complete, the extent of adsorption, if any, of the sulphate ions will indeed be very small since that concentration of sodium sulphate can only give 0.251 micro-mols of sulphate ions per gm. of barytes. Johnston and Adams (67) made a systematic study of adsorption of sodium sulphate on precipitated barium sulphate and they found an adsorption of 0.029 millimols of sulphate ions per gm. of barytes. This is about a hundred times greater than the first value (0.251 micro-mols.); i.e, either the surface of the present barytes is not

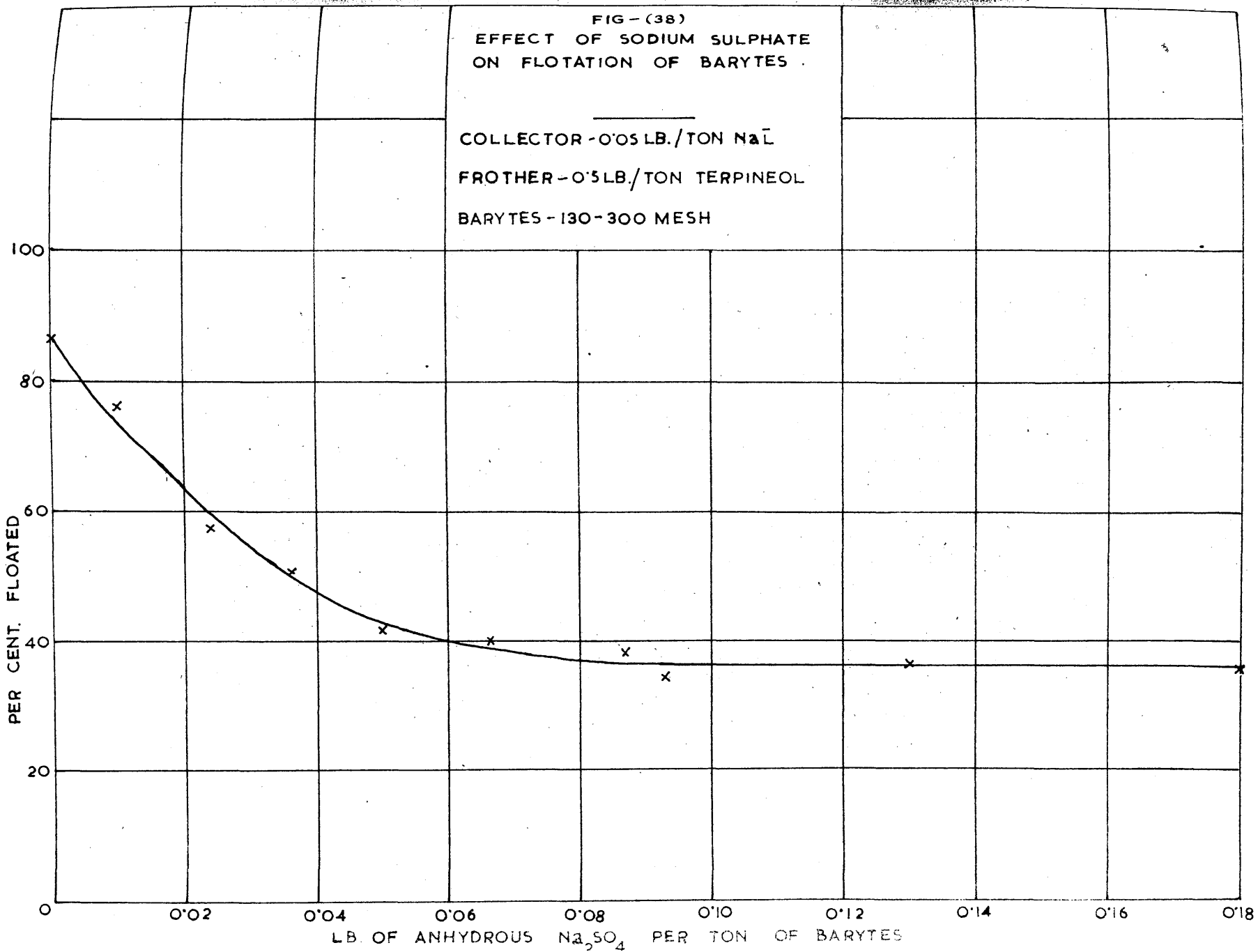


FIG – (38)
EFFECT OF SODIUM SULPHATE ON FLOTATION OF BARYTES.
COLLECTOR - 0·05 LB./TON NaL
FROTHER – 0·5 LB./TON TERPINEOL
BARYTES - 130 - 300 MESH
PER CENT. FLOATED
100
80
60
40
20
0
0·02
0·04
0·06
0·08
0·10
0·12
0·14
0·16
0·18
LB. OF ANHYDROUS Na_2SO_4 PER TON OF BARYTES

saturated yet with sulphate ions, or the surface area of the precipitated barium sulphate is about 100 times larger than that of the present barytes. The latter is more likely to be the reason for the high adsorption with precipitated barium sulphate.

Again, on the basis of a tetrahedral arrangement of oxygen atoms around the central sulphur atom, packed closely together, the cross-section of a sulphate ion is obtained as approximately 28 sq.$\mathring{A}^2$. Then, taking the specific surface of barytes as 1029.8 $cm.^2$ /gm., as obtained by the Lea and Nurse method and converted into gas adsorption value (see p.159), and the Avogardro's Number as 2.03×10^{23}, the formation of monomolecular layer of sulphate ions on barytes would require 1.811 micro-mols. This shows that even if all the sulphate ions from 0.08 lb./ton sodium sulphate were consumed in adsorption, only a fraction of the mineral surface will be covered.

It may be generally concluded that sulphate adsorption takes place resulting in the laurate ions being unable to adsorb on those points on the mineral surface where sulphate ions are present. Since sodium sulphate was added at the same time as sodium laurate, it seems that the sulphate ions are adsorbed in preference to the laurate ions and that this preferential adsorption increases with increase in concentration of sodium sulphate in solution.

Effect of Cations

Barium Ion.

Like sulphate ion, barium ion is common to the

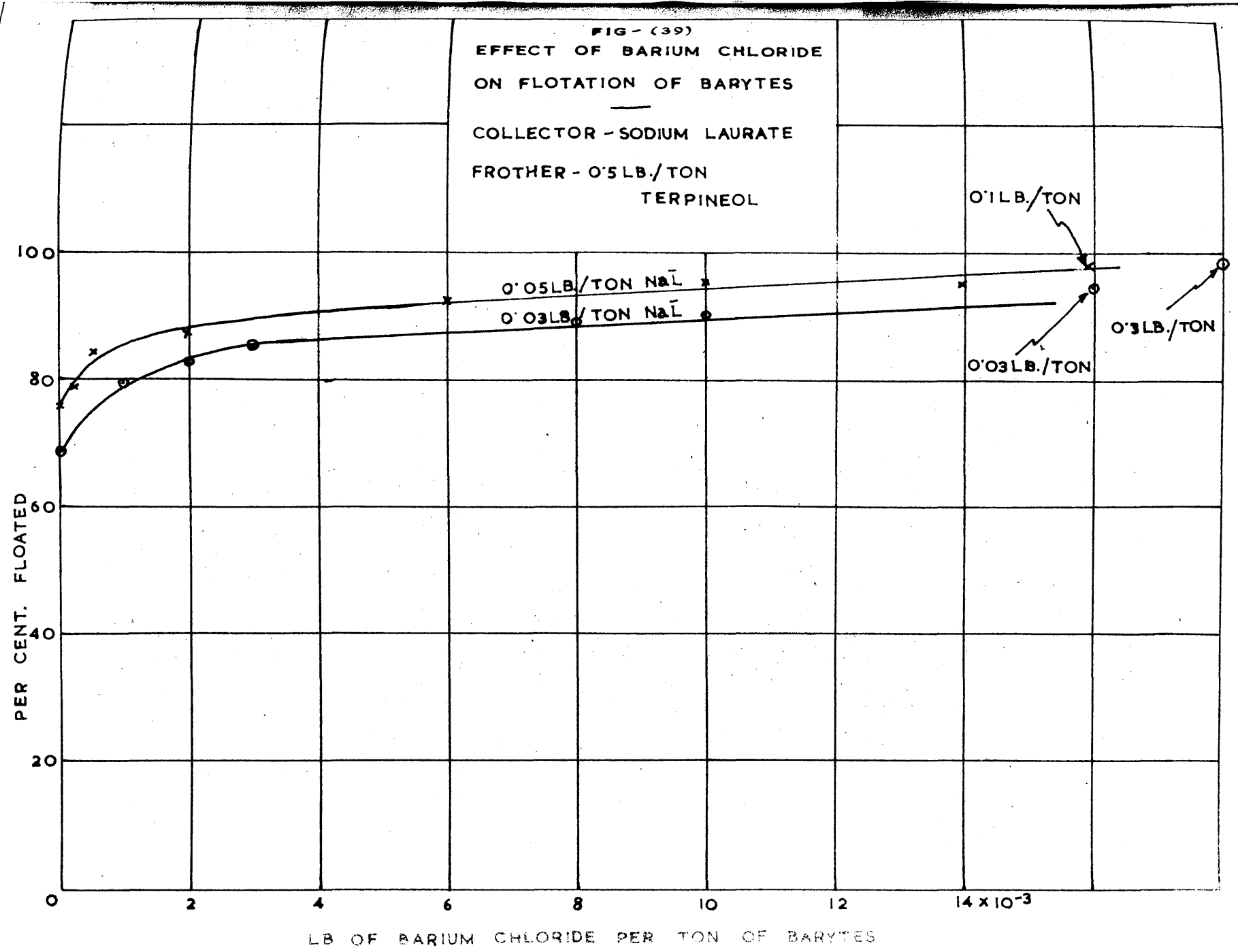


FIG - (39)
EFFECT OF BARIUM CHLORIDE
ON FLOTATION OF BARYTES
COLLECTOR - SODIUM LAURATE
FROTHER - 0·5 LB./TON
TERPINEOL
0·1 LB./TON
0·05 LB./TON NaL
0·03 LB./TON NaL
0·3 LB./TON
0·03 LB./TON
100
80
60
40
20
0
2
4
6
8
10
12
14 x 10⁻³
PER CENT. FLOATED
LB OF BARIUM CHLORIDE PER TON OF BARYTES

crystal lattice of barytes. To determine its effect on the flotation of barytes, a frother-collector solution containing 0.393 gm. of hydrated barium chloride (A.R.) in 50 cc. was first prepared and different volumes were added to 75 cc. of frother-collector solution in the flotation cell by means of a micro-pipette. Two different concentrations 0.05 lb./ton and 0.03 lb./ton, of sodium laurate was tested. In both frother-collector solutions, the concentration of terpineol was 0.5 lb./ton. The pH values of all the solutions were found to be nearly constant at pH 5.60.

The results, shown in Fig. (39), indicate that an activation takes place and that the relation between recovery and concentration is the same for both solutions in the concentration range tested. Considering the lower curve for 0.03 lb./ton sodium laurate, the concentration at which the activation starts, i.e. between zero and 2×10^{-3} lb. $BaCl_2$ per ton of ore, and the concentration at which the recovery reaches almost 100 per cent., i.e. 0.3 lb./ton, are very far apart. The activation by barium ions may, therefore, be considered as a slow process compared to other ionic effects described in this chapter.

Hälbich (68) had investigated the influence of various salts on the flotation of barytes using 150 gm. per ton of a collector rich in sodium lauryl sulphate (Utinal HC). He found that the activation was weak and that the recovery of barytes remained constant at about 70 per cent. even though the concentration of barium chloride was increased from 300 to 3000 gms. per ton. (i.e., from 0.66 to 6.6 lb./ton.).

Activation by barium ions in the flotation of barytes with nonylic acid was reported by Held and Dyachkov, who found that maximum adsorption occurs at 0.005 gm. equivalent of barium per litre of solution and at pH 4.57 from any solution, with the flotation remaining practically constant up to pH 11. If 0.3 lb./ton barium chloride for 0.03 lb./ton sodium laurate solution were assumed to represent approximately the concentration at which maximum flotation was attained, the concentration in water is obtained as 0.00051 gm. equivalent per litre which is only 1/10 th. of the above value for maximum adsorption.

Again, as in the case of sulphate ions, taking the ionic radius of barium as 1.43 Å, specific surface of barytes as 1029.8 $cm.^2/gm.$, and Avogadro's Number as 2.03×10^{23}, the amount of barium ions required for unimolecular adsorption on barytes is obtained as 7.90×10^{-6} gm. mols. per gm. of barytes. 0.3 lb./ton barium chloride, assumed above as the concentration for maximum flotation, gives 0.647×10^{-6} gm. mols of barium ion per gm. of barytes. Thus, a conclusion similar to the one arrived at with sulphate ions may be made:- that nearly 100 per cent. recovery or maximum activation may be achieved without the formation of a saturated layer of barium ions on the surface of barytes.

The activation by barium ions can be explained in the same manner as the depression by sulphate ions. The adsorbed barium ions will be situated opposite the sulphate ions of the crystal lattice, thus leading to the creation of more 'active

centres" on which more laurate ions can be adsorbed.

Wark (3) regarded this type of activation by barium ions as an instance supporting his "adsorption solubility product" theory. According to this conception, adsorption will occur if the product of concentrations of the metal and the collector ions exceed a certain value which is less than the normal solubility product. If the solubility of barium laurate is taken as 0.08 gm. per 100 gm. of solution, then the solubility product of this salt is 3.81×10^{-3}. The product of the barium and laurate ions in solution at 0.3 lb./ton barium chloride was calculated to be 3×10^{-8} assuming complete ionisation of sodium laurate in this very dilute solution. Hence the "adsorption solubility product", if reached at this concentration, must be considerably less than the actual solubility product in this particular case.

Ferric Ions.

Iron, in the form of oxides, is one of the major impurities in barytes ore. Previous investigators have found that it had apparently no influence on the flotative properties of the barytes which contained it even when the ore is stained badly by iron. This may be due to the extremely slow rate of solubility in water of the iron oxides left in the ore grains after leaching with hydrochloric or sulphuric acid. Iron, moreover, enters as an external impurity in most flotation pulps during the milling operations. It was, therefore, decided to find out the effect of ferric ions on the flotation of barytes.

Ferric chloride was used first to provide ferric ions in solution. A frother-collector solution (0.0447 gm. of terpineol and 0.0045 gm. of sodium laurate dissolved in 1 litre of water, and ~~This is~~ equivalent to 0.5 lb./ton and 0.05 lb./ton respectively when 75 cc. of this solution were added to 15 gms. of barytes in the cell) containing 6.705 gms. of 'anhydrous' ferric chloride in 100 cc. was prepared and added varying quantities to 75 cc. of the same frother-collector solution in the flotation eell by means of a micropipette. As 0.01 cc, of this solution was found to depress the flotation to a considerable extent, further dilutions with the frother-collector solution were made and the flotation tests continued. The points in the steep gradient of the curve in Fig. (41) were obtained by using an iron solution prepared by diluting the above original iron solution a hundred times.

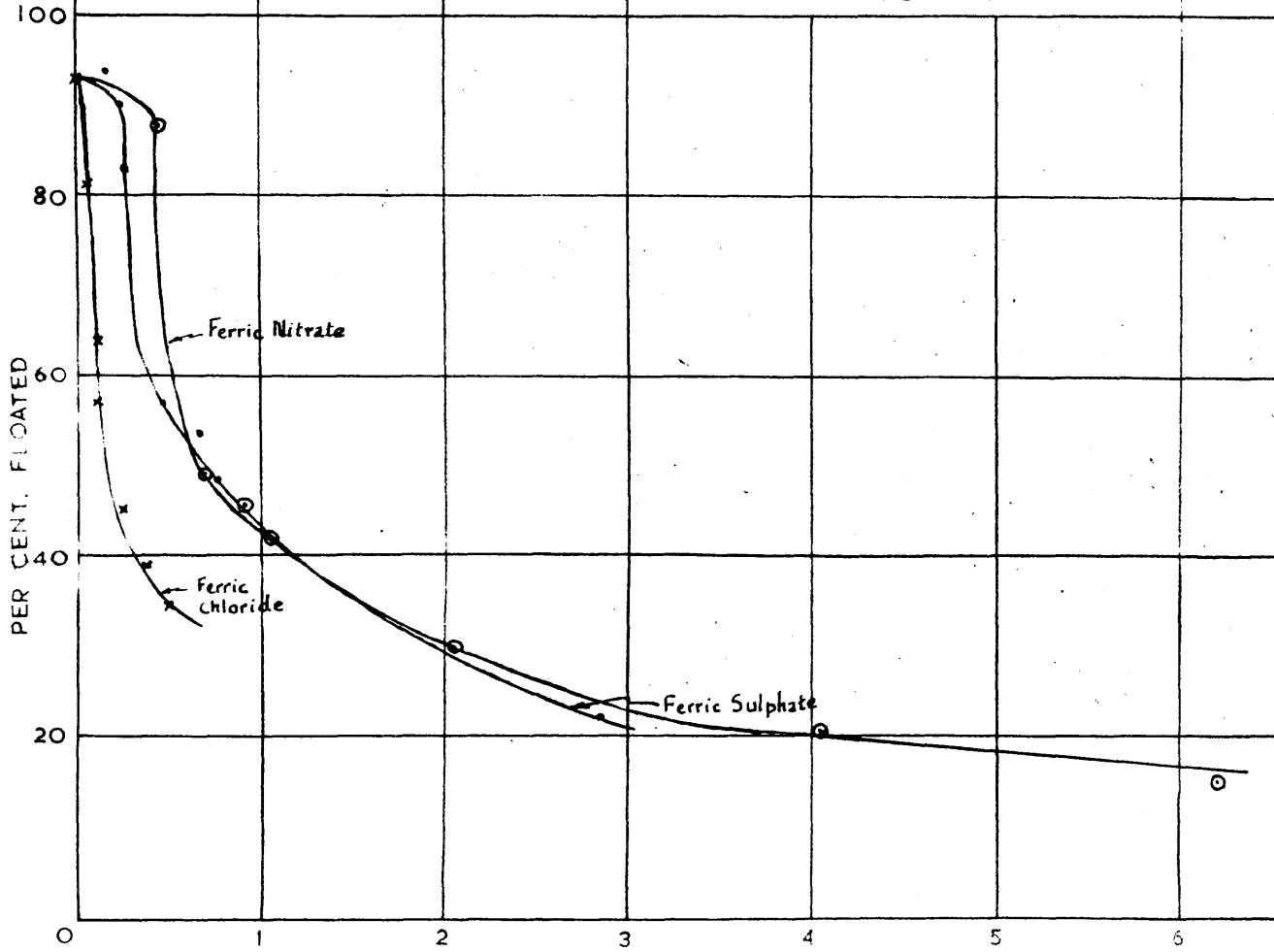
The actual quantity of ferric iron added in each test was determined by estimating the concentration of ferric iron in the solution obtained by diluting the original solution a hundred times. For this, the thiocyanate colorimetric method was used.

To 1 cc. of the iron solution were added 4 cc. of concentrated hydrochloric acid, 40 cc. of distilled water and 5 cc. of 4N potassium thiocyanate solution making up the total volume to 50 cc.. The colour obtained was compared with that of a standard ferric ammonium sulphate solution (0.216 gm. of ferric ammonium sulphate and 2.5 cc. concentrated

FIG - (40)

EFFECT OF FERRIC SALTS ON FLOTATION OF BARYTES

COLLECTOR - 0.05 LB./TON NaL SOL.
FROTHER - 0.5 LB./TON TERPINEOL
BARYTES - 130 - 300 MESH



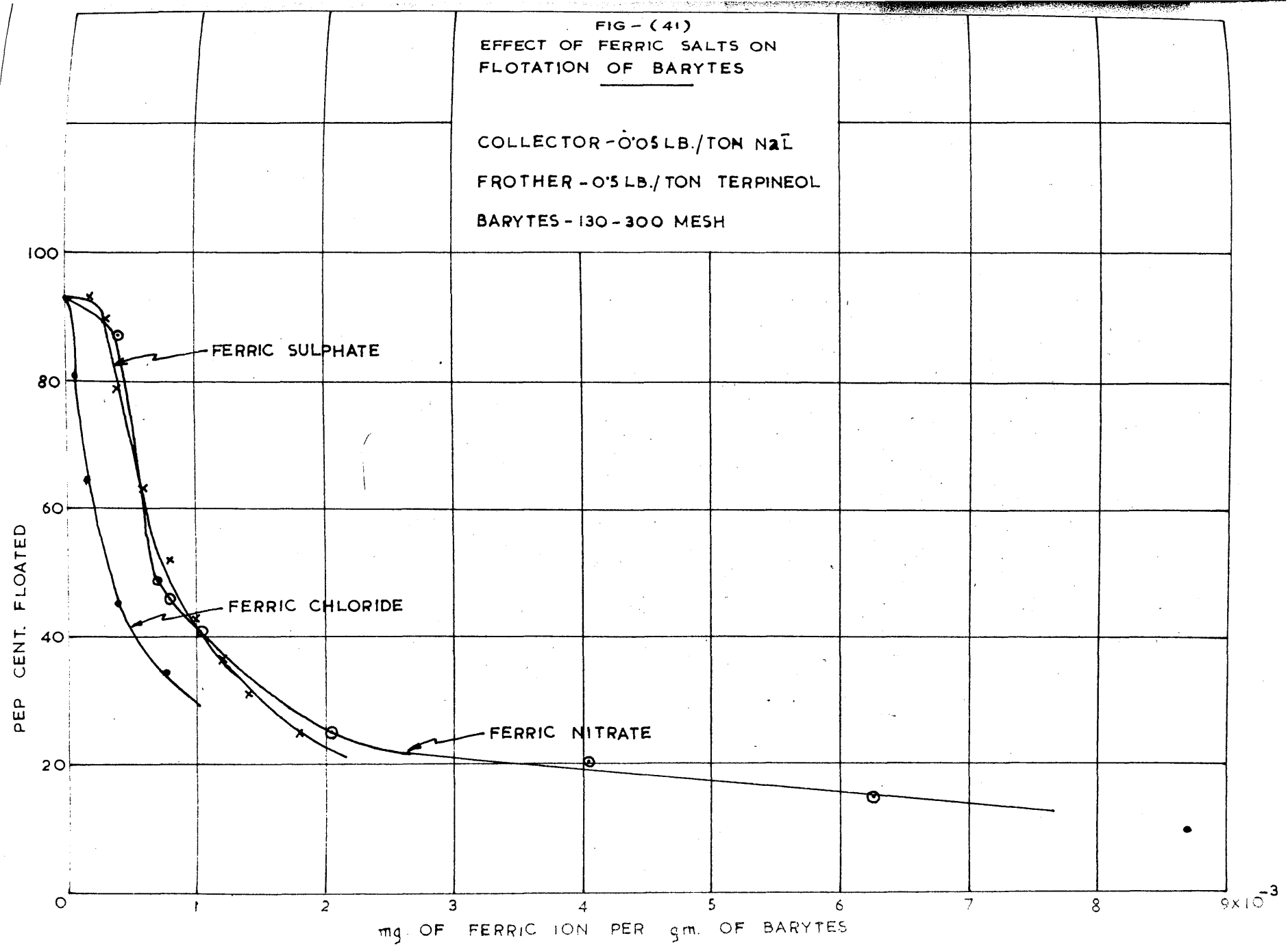


FIG – (41)
EFFECT OF FERRIC SALTS ON
FLOTATION OF BARYTES
COLLECTOR – 0·05 LB./TON NaL
FROTHER – 0·5 LB./TON TERPINEOL
BARYTES – 130 – 300 MESH
FERRIC SULPHATE
FERRIC CHLORIDE
FERRIC NITRATE
PER CENT. FLOATED
100
80
60
40
20
0
1
2
3
4
5
6
7
8
9x10⁻³
mg. OF FERRIC ION PER gm. OF BARYTES

hydrochloric acid in 250 cc. of solution) containing 0.1 mg. of ferric iron in 1 cc.. A Hilger Spekker (No.H.$\frac{560,301}{47848}$) with 8 cc. solution cells and a blue-green filter was used in this and in all subsequent determinations for comparing colours. Other ferric iron concentrations were calculated from this value.

Similar tests were then carried out with ferric nitrate and ferric chloride to see if the acid radical exert any influence on the effect due to ferric ions. Fig.(40) gives the variation in recovery with different concentrations of ferric salts expressed in lbs. per ton of ore., while in Fig. (41) the results are expressed on the basis of mg. of ferric ion per gm. of barytes, for reasons that will be apparent in the following discussion.

Although the depressing power of each of the three ferric salts is not very different from that of the other two, it can be said that the depression is greatest with ferric chloride followed by the sulphate and nitrate in order. The same behaviour was found by Keck and Jasberg (69), in the flotation of magnetite with 0.08 lb./ton sodium oleate solution. This cannot be related to the solubilities of the salts formed between barium ions of the lattice and the anions in solution, i.e., Cl^-, SO_4^{--}, and NO_3^-, since barium sulphate is the only "insoluble" salt of the three that can be formed. Also, it cannot be related to the order of adsorption of these anions on barytes for according to Weiser and Sherrick (70) nitrate ions are adsorbed by barium sulphate to a greater extent than

the chloride ions, being 8.48 gm. mols and 0.125 gm. mols respectively per 100 mols. of barium sulphate.

It is not understood in the depression by ferric sulphate whether the effect is wholly due to the ferric ion or to the combined effect of ferric and sulphate ions. From Fig. (38), if 0.08 lb. of sodium sulphate per ton of ore be taken as the lowest concentration required for complete depression of flotation, the equivalent sulphate ion concentration can be calculated as 1.52 mg. per gm. of barytes. Similarly, from Fig. (41), taking 3 mg. of ferric ion per gm. barytes as the lowest concentration for complete depression, the equivalent sulphate ion concentration is 7.87 mg. per gm. of ore. However, from the almost identical nature of the variation in recovery of barytes with concentration of ferric ion, as indicated by the curves in Fig. (41) it appears that the anions here play a relatively small part in the depression. Again, the action of the sulphate ion is probably of less importance than that of either the hydrogen ion or ferric ion at these low pH values.

For the sake of comparison, Hälbich's work (68) on depression of barytes by ferric chloride may be mentioned. Using 0.33 lb./ton sodium lauryl sulphate as collector, 0.44 lb./ton ferric chloride gave 68.4 per cent. recovery and 6.6 lb./ton gave 25.4 per cent. recovery. Evidently, the depressing power of the cation varies with the collector as well, being relatively greater with sodium laurate than with sodium lauryl sulphate.

FIG – (42)

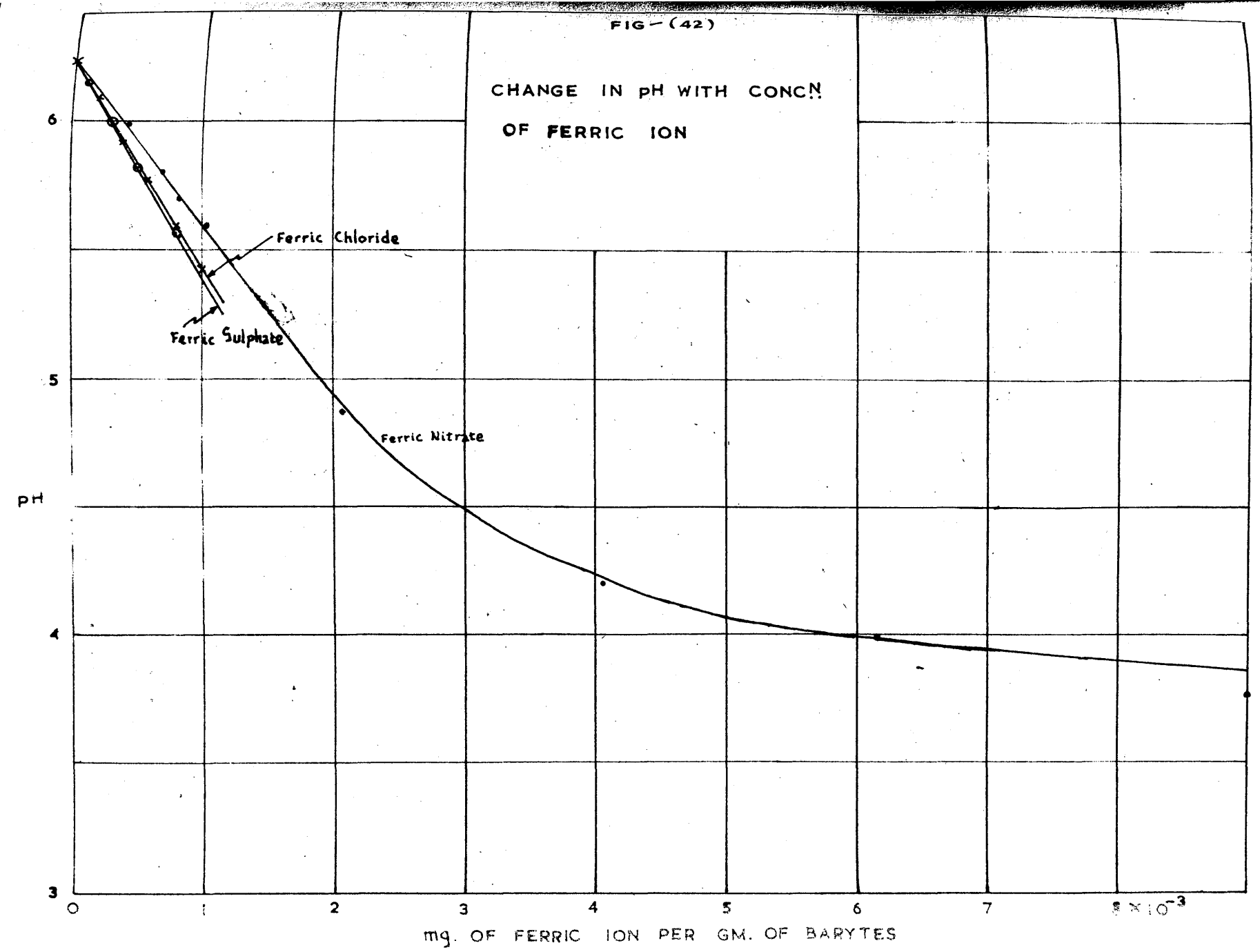
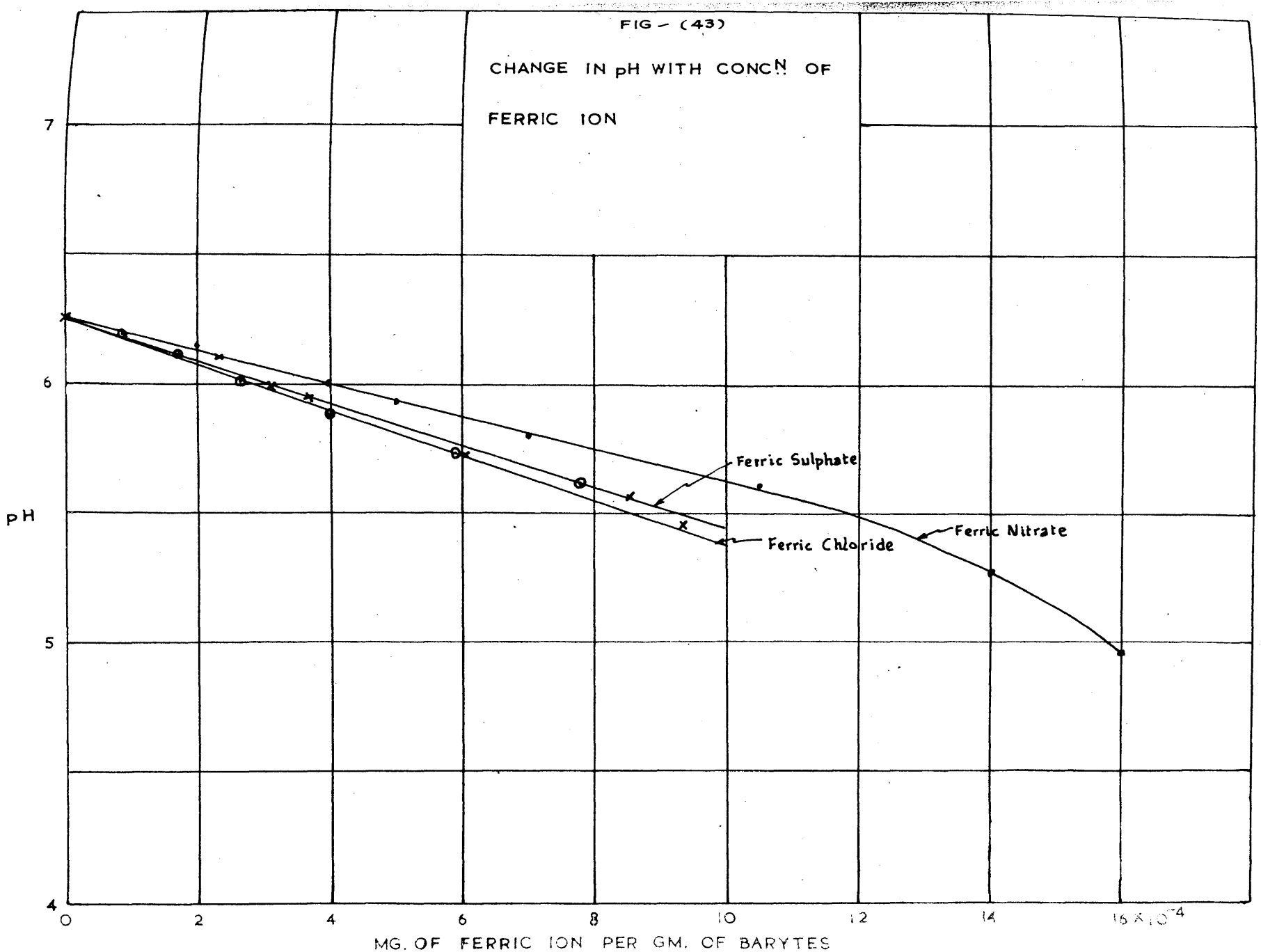

CHANGE IN pH WITH CONCN
OF FERRIC ION
Ferric Chloride
Ferric Sulphate
Ferric Nitrate
pH
6
5
4
3
0
1
2
3
4
5
6
7
8 × 10⁻³
mg. OF FERRIC ION PER GM. OF BARYTES

FIG – (43)

CHANGE IN pH WITH CONCN OF FERRIC ION



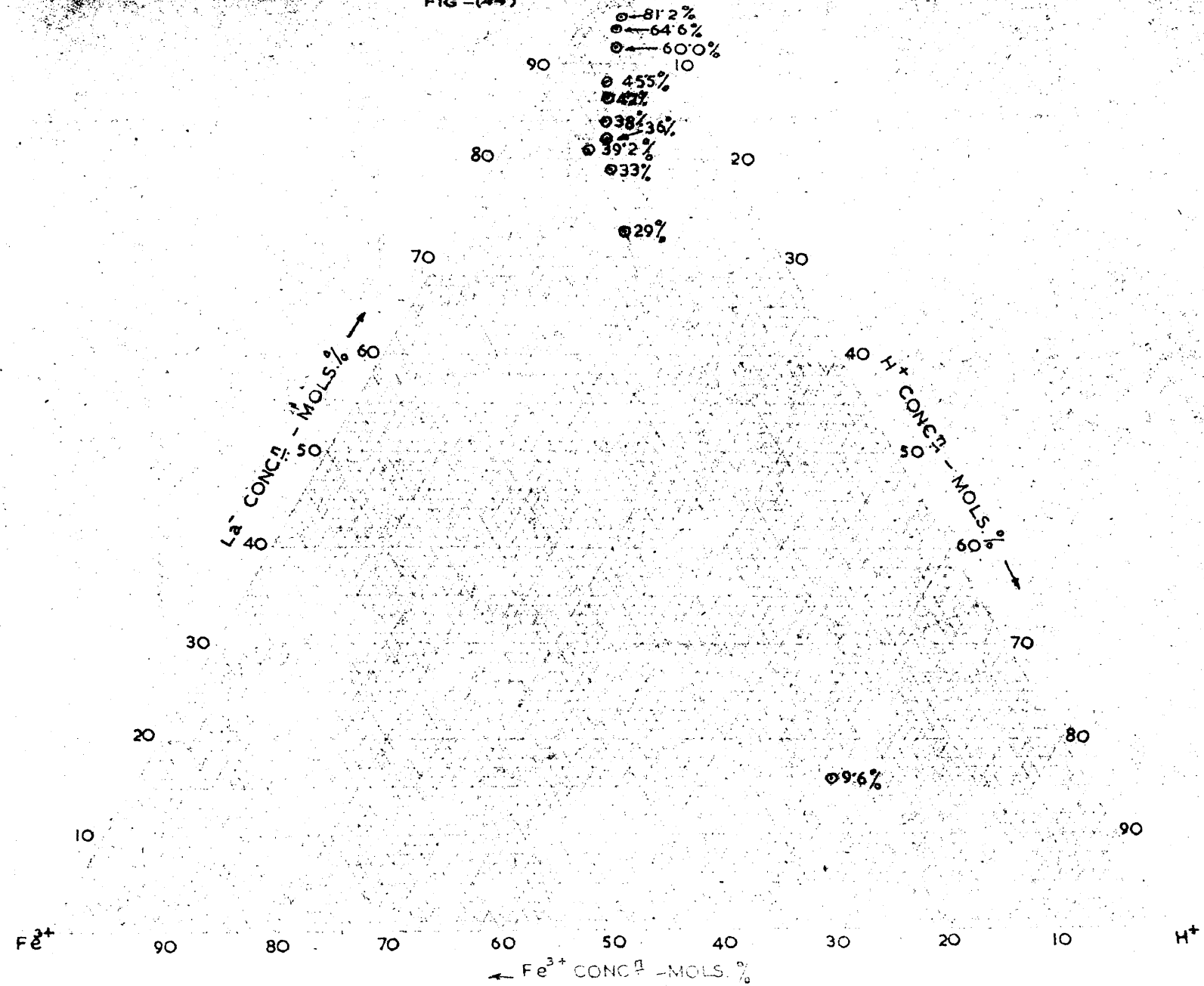
According to Rogers and Sutherland a depressant should be of the same polarity as the collector ion. Here the laurate ion is negatively charged whereas the ferric ion is positively charged. This seems to be an exception to Rogers and Sutherlands' Principle, and in direct contrast to the well known activation of silica by ferric ions in flotation with long-chain paraffin salts.

In the above flotation tests, no attempt was made to keep the pH constant. The pH of the frother-collector solution was near that of the distilled water used for preparing the solution and the ferric salt solutions were, in general, of acid pH. The pH of the iron solutions accordingly varied with the concentration of salt added. A study of this variation was made by preparing each solution again exactly in the same manner as in the flotation tests except that there was this time no mineral present. The results are given in Fig. (43) and (42). A wider range of ferric ion concentration is shown in Fig. (42) to indicate in more detail the case of ferric nitrate. It can be seen that in the region where the recovery falls rapidly with ferric ion concentration, i.e., from zero to 2×10^{-3} mg. per gm. barytes, the pH value is inversely proportional to ferric ion concentration. From these curves, the pH of the solutions tested with ferric ion concentrations, as given in Fig. (41), can be obtained.

Triangular Diagrams.

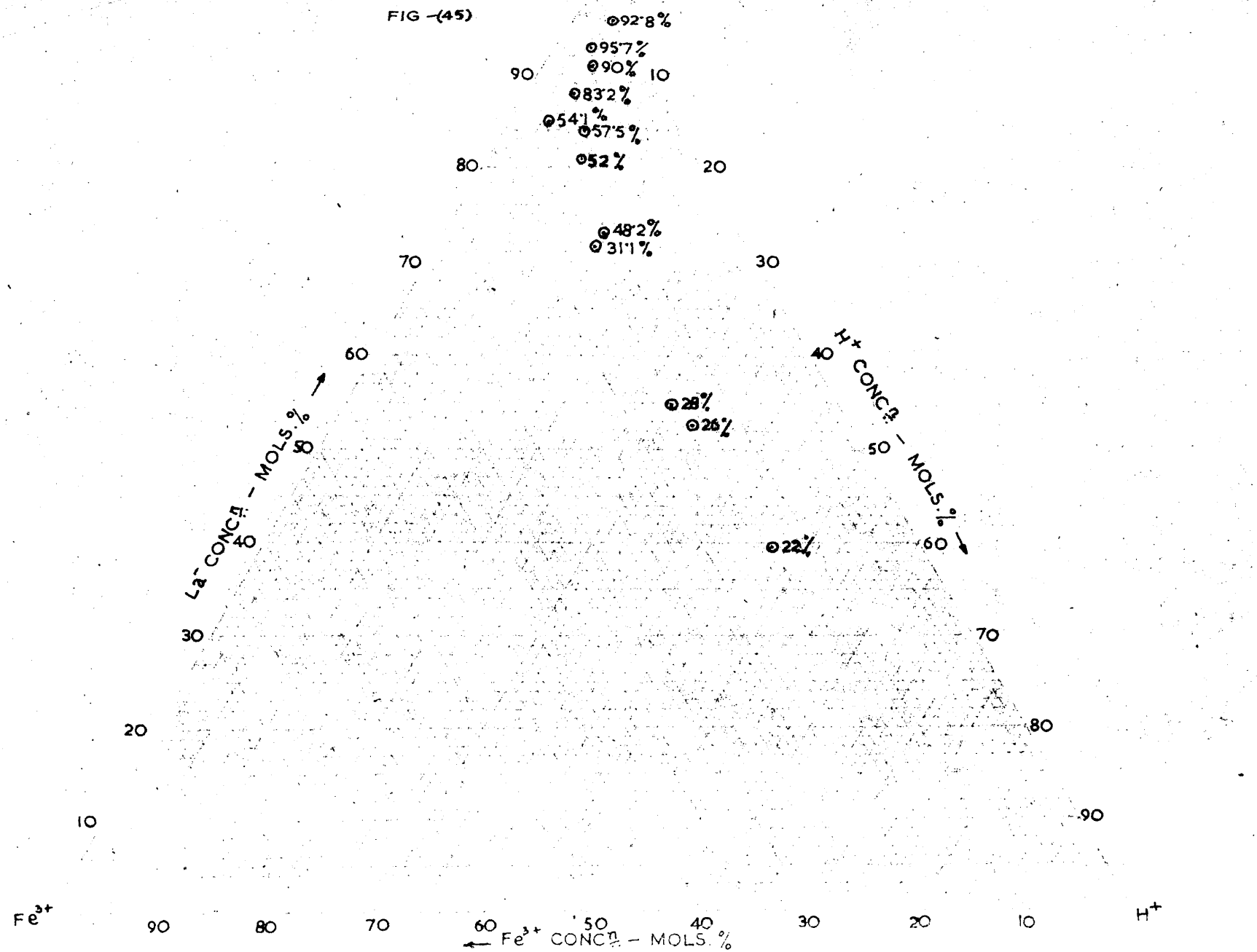
In the depression by ferric salts, the three ions, viz., laurate ions, hydrogen ions and ferric ions, are known

FIG –(44)



FLOTATION OF BARYTES WITH NaL AS COLLECTOR
DEPRESSANT – FERRIC CHLORIDE

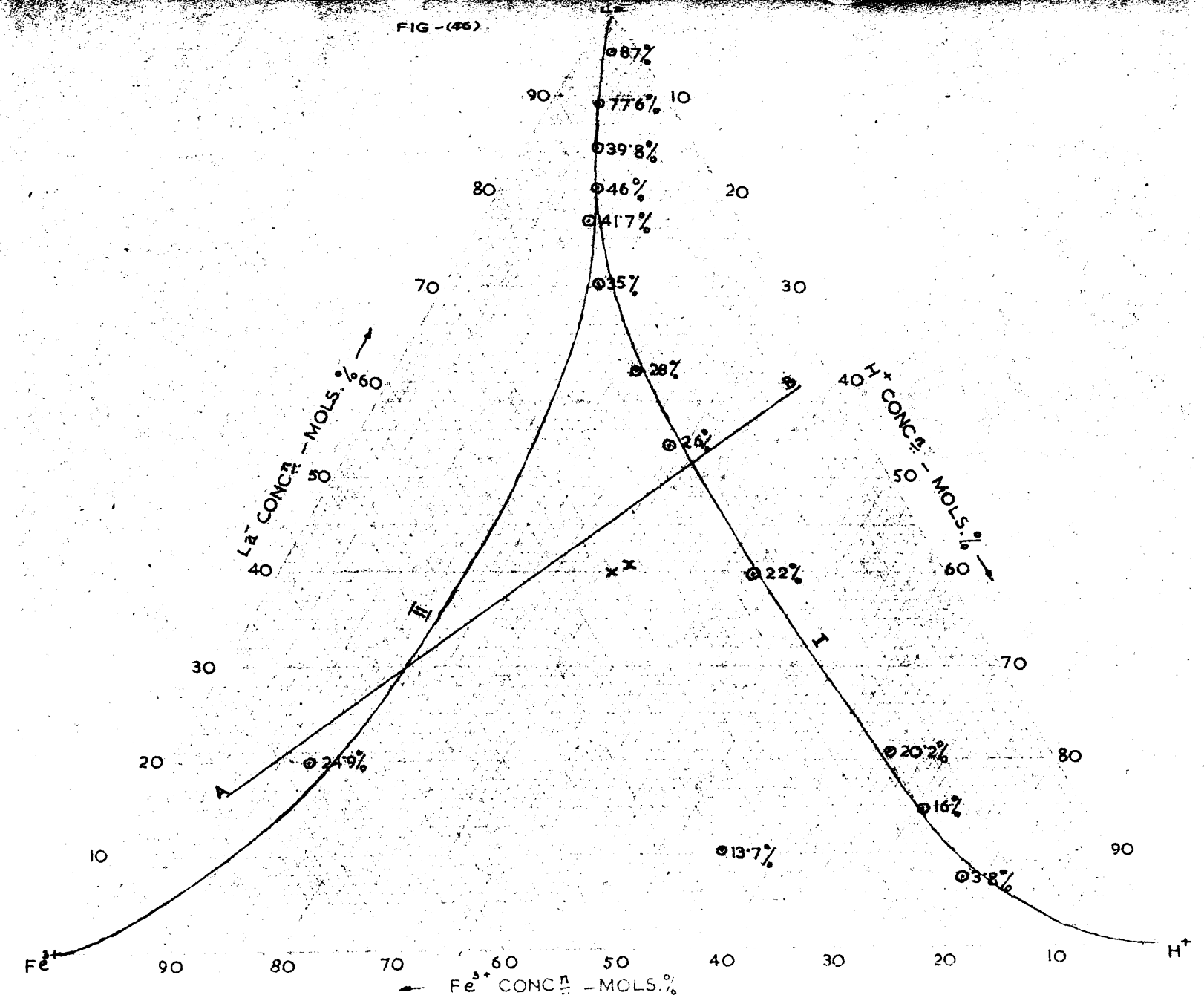
FIG -(45)



FLOTATION OF BARYTES WITH SODIUM LAURATE

DEPRESSANT – FERRIC SULPHATE

FIG -(46)



FLOTATION OF BARYTES WITH SODIUM LAURATE

DEPRESSANT — FERRIC NITRATE

to affect the flotation. At the outset, it can be postulated from results already obtained that a relatively high proportion of laurate ions will result in a high recovery while a preponderance of either of the other two ions will cause a depression. The pH of the ferric salt solutions tested varies from about 6.2 to 5.3 as seen from Fig. (42) and (43). If it were assumed that the effect of pH on flotation with sodium laurate is approximately the same as with lauric acid, analogous to the case of sodium caprylate and caprylic acid solutions (p. 103, Ch. VII.), then the possible change in recovery within that pH range is about 10 per cent. from Fig. (36); that is, the depressing action due to the increase in hydrogen ion concentration is probably only a small proportion of that due to ferric ions.

Knowing the concentrations of sodium laurate, ferric ions and pH of the solutions, the concentration of each of the three ions in gm. molecules per litre was calculated. From the total number of gm. molecules present in 1 litre of solution, the respective mol. percentages were obtained. In Figs. (44) to (46), the composition of each solution with respect to the three ions was represented by a point in the triangular diagram with the recovery value beside it. A separate diagram was drawn for each, Ferric Nitrate, Chloride and Sulphate, to avoid overcrowding the points at the top corner.

The following inferences may be drawn from the diagrams:-

1) ... The high recovery values from about 30 per cent. to 100 per cent. are only obtained with the solution compositions represented by points near the top corner where the laurate ion concentration is generally above 70 mols. per cent..

2) ... From the trend of the points for ferric nitrate, it seems that the curve (I) is the equivalent of the curve for the same salt in Fig. (41). Curve (II) is also possible. Along curve (I) laurate ion concentration decreases while the hydrogen ion concentration increases and the ferric ion concentration varies between zero and 20 mols. per cent. Instead of this, if the hydrogen ion concentration were to be kept within zero to 30 per cent. mols. while ferric ion concentration was increased gradually, a depression could still be obtained as predicted by curve (II).

3) ... There could also be constant recovery lines as indicated by the line AB. As we go from A towards B, the laurate ion and the hydrogen ion concentration increase while the ferric ion concentration decreases. The inclination of the line will depend upon the relative effect of each of the two depressing ions.

4) ... In these three particular cases, none of the solutions tested is capable of giving a point in the middle portion of the triangle. This is probably controlled by the pH of the solution. For example, take the point x in Fig. (46) for ferric nitrate. For the fixed concentration of laurate ions used, the concentration of ferric ions should be 4.284×10^{-3} mg./gm. of barytes and the pH should be 5.82, but from Fig.(43)

it can be seen that the pH of a solution containing that amount of ferric ions is 4.12.

It is difficult to decide whether the depressing action is due to the reaction between the ferric salt and sodium laurate in solution or to the prevention of the collecting action of adsorbed laurate ions by adsorption of ferric ions. If ferric laurate were formed in solution then 0.05 lb./ton sodium laurate used would need 2.18×10^{-3} mgm. of ferric ion per gm. of barytes. This concentration corresponds to about 25 per cent. recovery of barytes which can be located at a point at the foot of the steep part of the curves in Fig. (41). Kraeber and Boppel assumed that, in the activation of quartz by ferric salts, reaction took place between the ferric salt and the sodium salt of Ricinol-sulphonic acid - $CH_3.(CH_2)_5.CH.(O.SO_3Na).CH_2.CH=CH.(CH_2)_7COONa$ which was used as collector while the excess were adsorbed on the quartz surface. If ferric laurate was assumed to be undissociated in solution and if it were merely a case of reaction between ferric salt and sodium laurate, there should be no abstraction of ferric ions by barytes, but if both adsorption and reaction were to occur, more ferric ions should be consumed than was needed for adsorption alone. To settle this issue, some experiments on adsorption of ferric ions were carried out as described below.

Adsorption of Ferric Ions on Barytes.

Variation with pH.

To determine the optimum pH for adsorption of ferric

ions, the variation with pH was first studied following the method adopted by Kraeber and Boppel (43) in their investigations on the adsorption of ferric ions on quartz. 10 gms. of purified natural barytes (130-300 mesh) were taken in a conical flask of 250 cc. capacity and 50 cc. of N/5000 $FeCl_3$ solution were added. The pH of the solution was adjusted to the desired value by adding dilute caustic soda, the volume of which was never allowed to exceed 2 cc. to prevent excessive dilution. A rough estimation of the pH of the resulting solution was made by means of pH test-papers. The contents of the flasks were shaken for two minutes and the solid was then allowed to settle for a minute. The supernatent layer was poured out into a clean dry beaker. For ferric ion determination, 10 cc. of the decanted solution were pipetted out into a 100 cc. beaker and to it were added 2 cc. N/10 HCl and 3 cc. of N ammonium thiocyanate solution. The colour intensities were compared by using the Hilger Spekker as before. The pH of the remaining solution was measured by means of a portable Cambridge pH meter (No. L.92781.).

Freshly prepared N/5000 $FeCl_3$ solution has a pH of about 4.6. Through the hydrolysis of ferric chloride in water, Kraeber and Boppel estimated that when equilibrium had reached in hydrolysis, the ferric chloride solution at pH 3.3 contained 80 per cent. of ferric hydroxide, i.e., ferric chloride is hydrolysed to a considerable extent even at very low pH values. The ferric hydroxide produced is in the form of a colloidal precipitate and as its settling rate is much

slower than that of the barytes powder, practically all of it was removed on decanting the supernatent layer after three minutes of contact. If a longer time of about ten minutes were allowed, the precipitate would have sttled on the powder and it would be almost impossible to separate the two by mechanical means.

As a check on the results, some of the samples, that showed appreciable adsorption, were washed twice with distilled water. The wash-water contained no iron according to tests with ammonium thiocyanate solution. 10 cc. of concentrated iron free hydrochloric acid, in three portions of 5 cc., 3 cc. and 2 cc., were next added to each of the samples to extract the adsorbed iron. Then the resulting solution was tested for iron as before. A blank experiment with the original barytes indicated that the iron originally in the ore could not be extracted with concentrated HCl in the cold. The iron removed, therefore, came entirely from the adsorbed layer. From the results in the following table, it can be seen that the quantity of ferric iron obtained from the barytes is approximately equal to the decrease in ferric ion content of the solution in contact.

TABLE (10)

pH of Solution	Ferric Ion adsorbed (gms./gm. of barytes)	
	From Barytes.	From Solution.
2.09	0.104×10^{-5}	0.147×10^{-5}
10.13	0.285 x ..	0.272 x ..
11.07	0.904 x ..	0.994 x ..
11.40	0.676 x ..	1.074 x ..

TABLE (11)

pH	1.79	2.09	7.68	10.13	11.07	11.40
Ferric ion adsorption mgm./gm.barytes	0.3×10^{-3}	1.32×10^{-3}	4.42×10^{-3}	5.32×10^{-3}	9.94×10^{-3}	10.74×0^{-3}

In the Table (II) are the quantities of ferric ion adsorbed at different pH values. These results indicate a marked increase in adsorption with increasing pH. Kraeber and Boppel, however, found that the adsorption of ferric ions on quartz reaches a maximum near the neutral pH and falls off on both the acid and alkaline sides. No such maximum was obtained with barytes. This might have been due to the initial ferric ion concentration of 3.48 mg. per litre being too low for maximum adsorption to occur. Later experiments revealed this to be true for at pH 4.78, at least 30 mg. per litre of ferric ions was required to achieve a saturated layer on the mineral surface.

Assuming the specific surface to be 1029.8 $cm.^2/gm.$, as determined by the Lea and Nurse method and converted into gas adsorption value by multiplying with the factor 1.9, and the ionic radius of ferric ion to be 0.67 Å, a monomolecular layer would require 0.678 mg. of ferric ions per gm. of barytes, which is about 60 times greater than the maximum value at pH 11.40 in Table (II). Hence a monolayer has not formed at any of the pH values tested.

At pH values above 2.00 colloidal ferric hydroxide was precipitated. It remained evenly mixed with the solution for a comparatively long time at pH values below 7 but as the alkalinity of the solution was increased, it ~~would~~ was found to settle more quickly. Therefore, although no optimum pH could be chosen for adsorption experiments, it is preferable to work at low pH values for practical reasons.

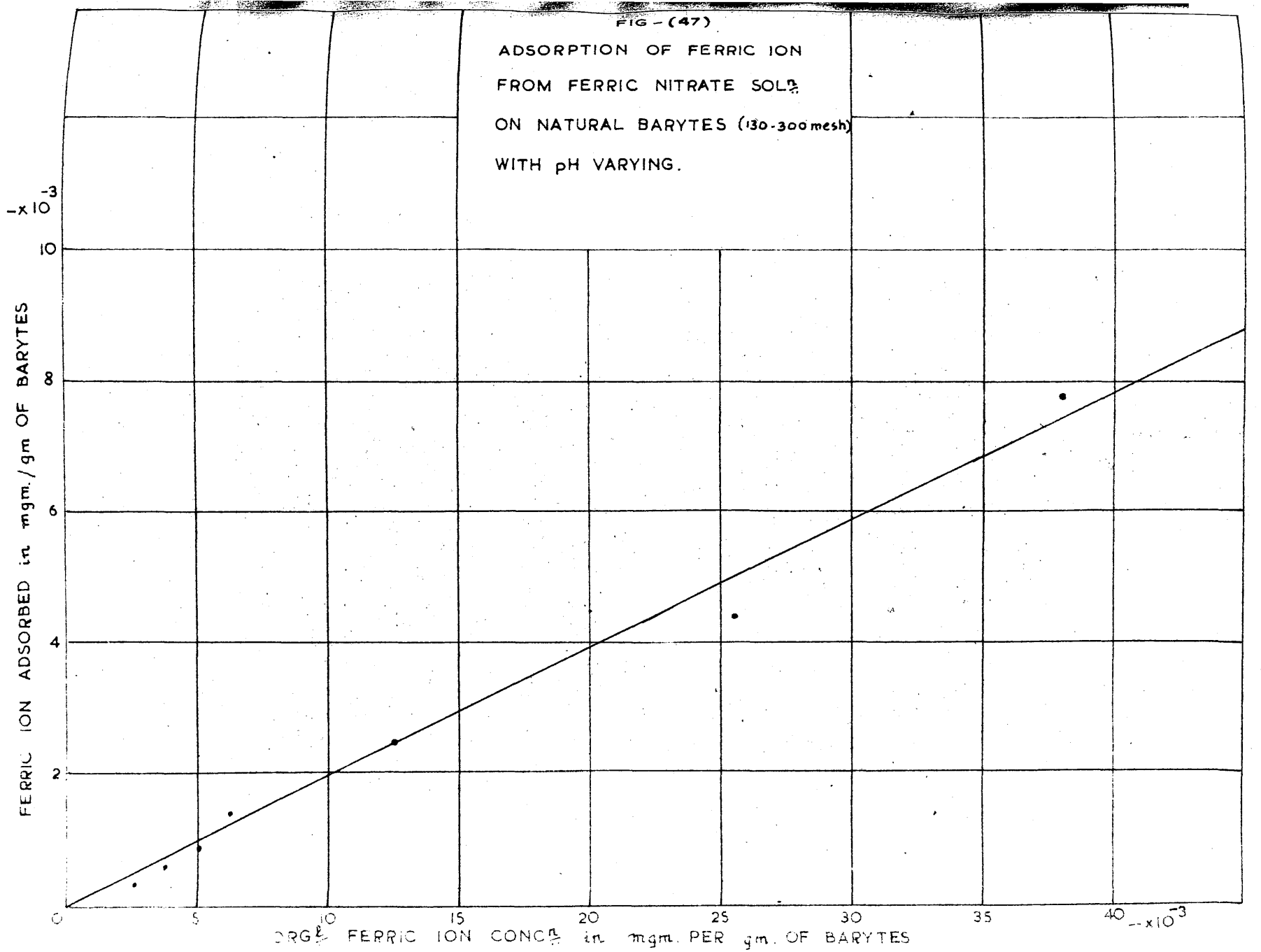
Adsorption with Varying Ferric Ion Concentration and pH.

As already stated, it is important to know whether any ferric ion is abstracted in flotation tests with ferric salts. For this, 150 cc. each of different concentrations of ferric nitrate in collector-frother solution (0.05 lb./ton sodium laurate and 0.5 lb./ton terpineol) was prepared exactly as in the flotation experiments. 75 cc. of each solution was put into the flotation cell with 6.6 cc. of barytes and the mixture stirred for three minutes. The solution was withdrawn by suction through the porous glass membrane of the cell and into a Buchner flask beneath. It was then tested for ferric ion content. The barytes sample used was dried and weighed. The difference in the ferric ion concentrations of the solution before and after contact with barytes gave the amount adsorbed. The pH Values of the solutions were also measured.

The results are plotted in Fig. (47). Within the concentration range examined, the adsorption is proportional to the original concentration. It should be noticed that the original concentration and not the equilibrium concentration is used here so as to enable a comparison to be made with the flotation results in Fig. (41). In the effective concentration range of up to 7×10^{-3} mg. of ferric ions per gm. of barytes, the adsorption is extremely low increasing from zero to about 1.5×10^{-3} mg. per gm. of barytes and it is, therefore, probable that ferric ions are adsorbed as such even although adsorption as ferric laurate or as counter ions to the laurate ions may also take place.

FIG – (47)

ADSORPTION OF FERRIC ION FROM FERRIC NITRATE SOLⁿ ON NATURAL BARYTES (130-300 mesh) WITH pH VARYING.



Comparison of Natural Barytes and Pure Barium Sulphate

Preparation of Pure Barium Sulphate Crystals.

The above preliminary investigations led to the belief that in order to understand fully the mechanism of depression by the ferric ions, a study should be made of the adsorption of ferric ions on pure barium sulphate with and without collector coating. As already stated, it is well-nigh impossible to free the natural barytes from iron impurities even when the ore is hand-picked unless the ore is reduced to a very fine state. Consequently, pure crystallised barium sulphate was prepared.

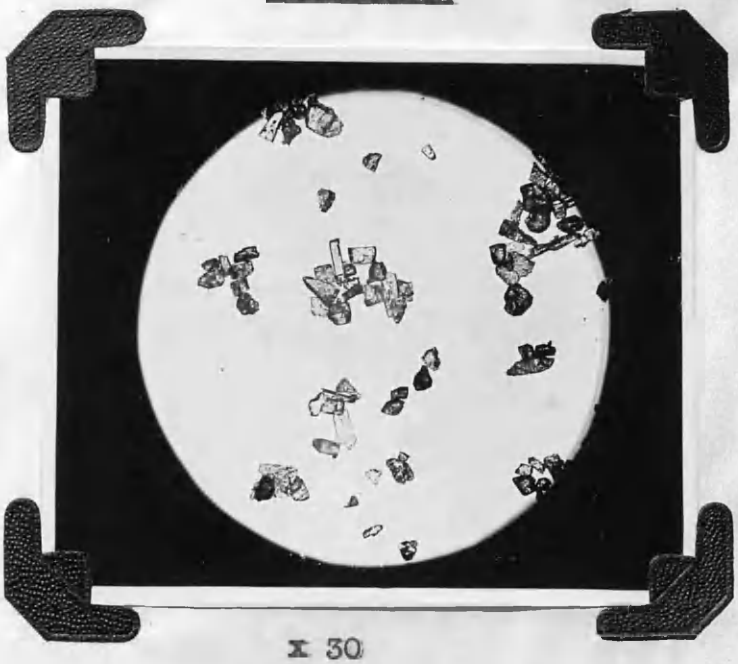
The method used was that of Buchanan and Heymann (71). Barium sulphate was precipitated at a very high dilution from A.R. barium chloride and A.R. sulphuric acid. The barium chloride solution was made up to 5 per cent. concentration by weight. The precipitate was filtered and dissolved in pure concentrated sulphuric acid. Although the solubility was supposed to be 15 per cent. by weight, nearly twice the volume of sulphuric acid required had to be added to dissolve all the barium sulphate. On evaporating the solution in a silica dish to a small volume, crystals of barium sulphate were obtained. After washing thoroughly with distilled water and decanting off the fine precipitate, the crystals were stored under water ready for use.

A spectroscopic examination revealed the analysis as given below:-

Constituents.

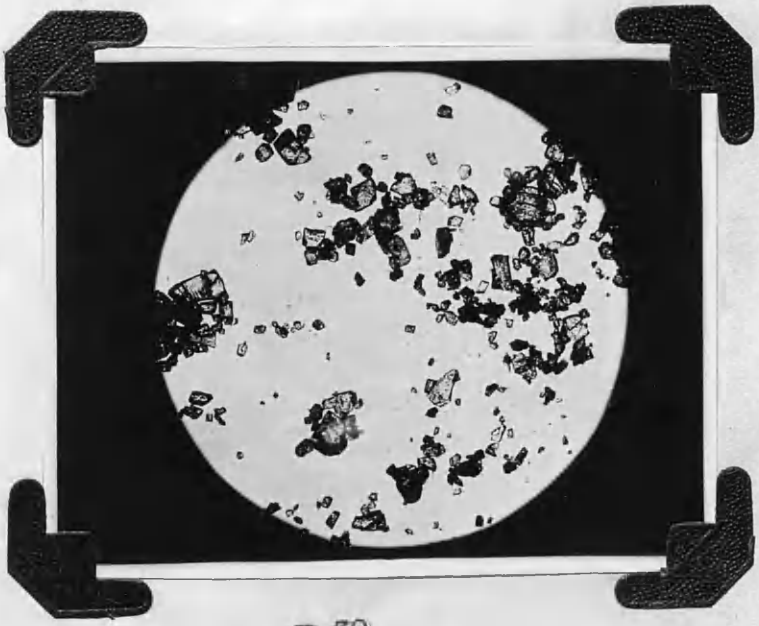
Al) .. each not more than 0.001 %

PLATE (II)



x 30

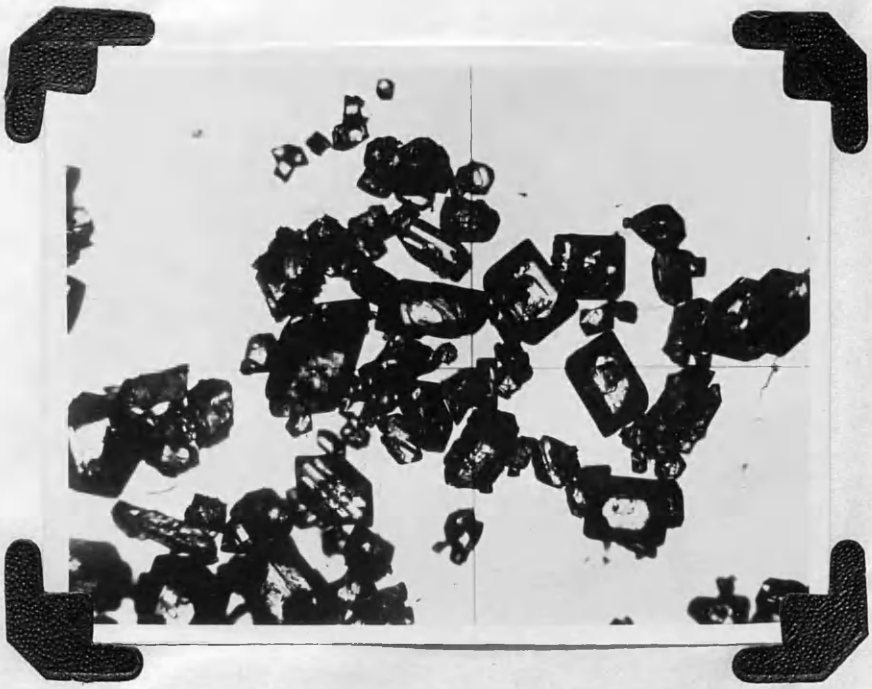
-120+150 MESH NATURAL BARYTES



x 30

-130+300 MESH NATURAL BARYTES

PLATE (III)



x20

GROUND PURE BARIUM SULPHATE

Constituents (Cont'd.)

Cu, Fe, Sr, Na ..... each not more than 0.001 %

Ca ..... less than 0.01 %

Total impurity about 0.01 %

Not present:- Si, Sb, Bi, B, Cd, Mg, Mn, K, Sn, and Zn.

About two thirds of the crystals were of 0.5 to 2.mm. diameter, the rest being less than 0.1 mm. diameter. Microphotographs of the synthetic and natural barytes particles are compared in Plates II and III. Although Buchanan and Heymann reported irregularities in the surfaces of synthetic barytes crystals as compared to the very regular surface of natural barytes, it was difficult to find such a difference from the microphotographs since both varieties appeared to have similar proportions of both regular and irregular particles.

Comparison of the Flotation of Natural Barytes and Pure Barium Sulphate.

Tests were carried out in the Hallimond Tube, to compare the flotation of pure barium sulphate with that of natural barytes. The recovery values at different concentrations of sodium laurate in solution were obtained for both substances. A solution containing 0.01 gm. of sodium laurate per litre of water was prepared first and then diluted with water to get lower concentrations. The results with pure barium sulphate of average particle size 340 microns and

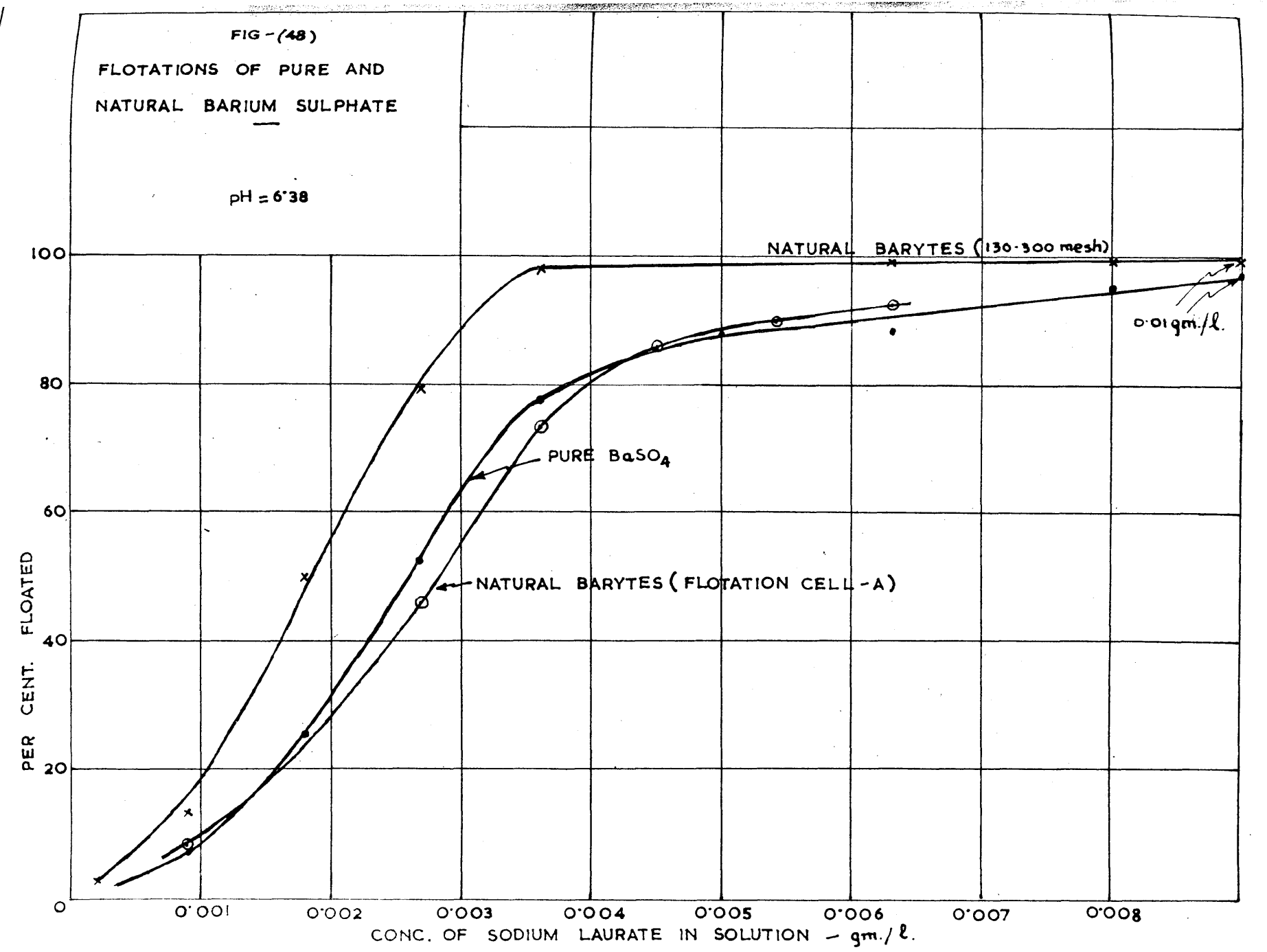


FIG - (48)
FLOTATIONS OF PURE AND
NATURAL BARIUM SULPHATE
pH = 6·38
NATURAL BARYTES (130-300 mesh)
0·01 gm./l.
PURE BaSO4
NATURAL BARYTES (FLOTATION CELL-A)
PER CENT. FLOATED
0
20
40
60
80
100
0·001
0·002
0·003
0·004
0·005
0·006
0·007
0·008
CONC. OF SODIUM LAURATE IN SOLUTION - gm./l.

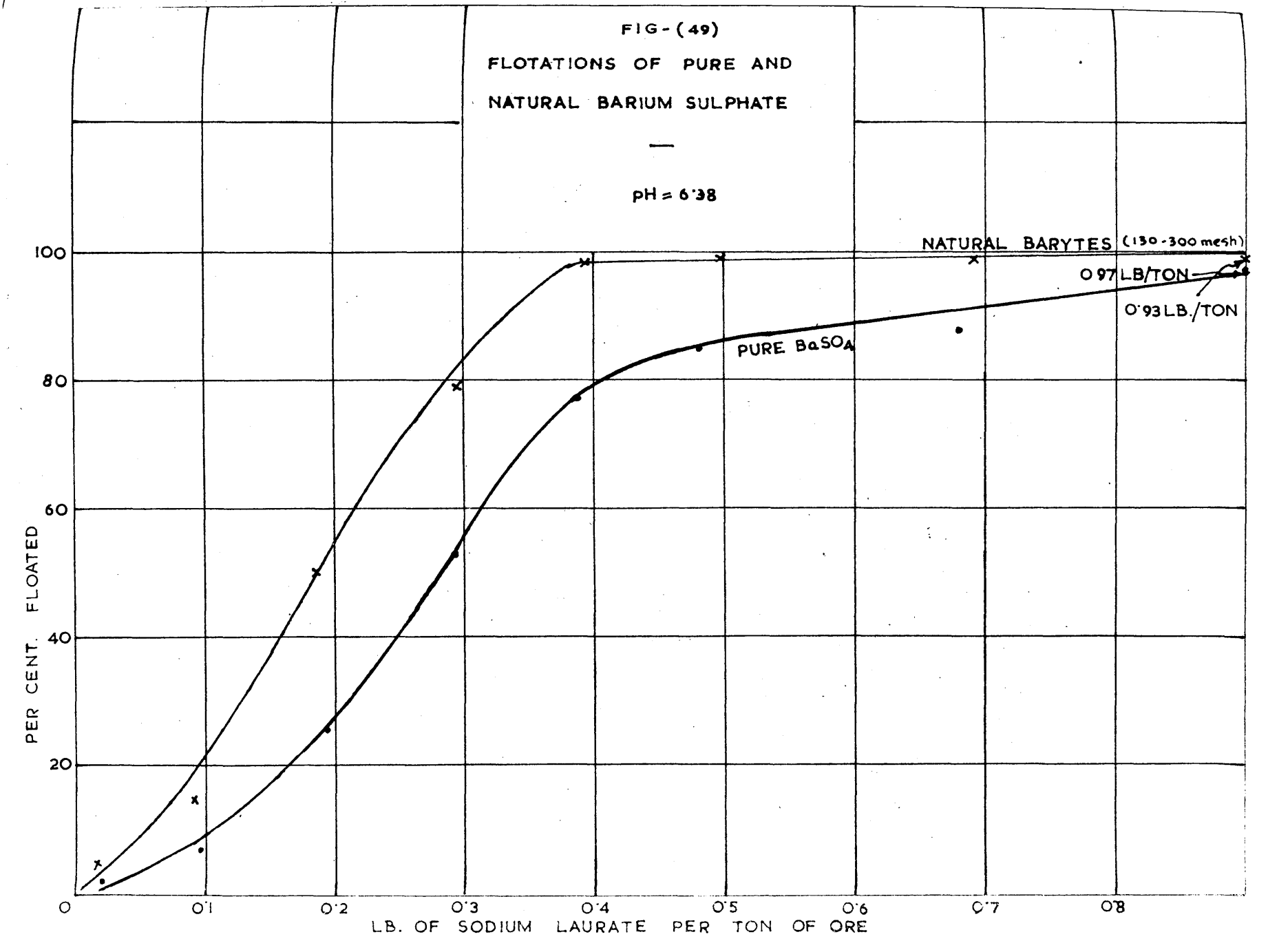


FIG-(49)
FLOTATIONS OF PURE AND
NATURAL BARIUM SULPHATE
pH = 6·38
NATURAL BARYTES (130-300 mesh)
0·97 LB/TON
0·93 LB./TON
PURE BaSO4
PER CENT. FLOATED
100
80
60
40
20
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
LB. OF SODIUM LAURATE PER TON OF ORE

natural barytes of size 130 mcrons (130-300 mesh) are given in Figs. (48) and (49). The concentrations are expressed in gms./l. in Fig. (48) and in lbs./ton in Fig. (49).

These results indicate:-

a) ... That although the two substances are of different particle sizes and specific surfaces, their floatabilities are almost identical. The slightly higher recoveries with the natural ore may be attributed to its higher specific surface.

b) ... That the effective concentration range expressed in lbs./ton., is about 10 times that obtained with the flotation cell (A) (compare Figs. (49) and (25)). This is simply due to the very high dilution ratio of about 0.83 gm. of ore to 40 cc. of solution in the Hallimond Tube compared to the 15 gms. of ore to 75 cc. of solution in the cell (A). In Fig. (48), the results for the curve (b) in Fig. (25) are represented by the dotted curve having converted the lbs./ton concentrations into gms./l.. This curve seems to be more in agreement with that of the pure barium sulphate rather than that of the same natural barytes. This may have been caused by the use of a higher pH of 6.38 in the Hallimond Tube (pH in cell (A) is 5.1). The significance of the present observation lies in the fact that in a laboratory flotation test the concentration of the collector in solution is more fundamental than its concentration with respect to the ore. The comparison of flotation in different cells should, therefore, be made on the basis of the concentration of the collector in water, especially as the latter determines the adsorption on the mineral and consequently its flotation.

Adsorption Tests.

The pure barium sulphate was ground under water in a clean porcelain mortar and washed thoroughly to remove slimes. The average particle size of the ground barium sulphate was found to be 0.34 mm. (340 microns). This was much larger than the average size of either 120-150 or 130-300 mesh natural barytes.

The procedure was to take 5 gms. of pure barytes, dried at 120°C in a vacuum oven for 5 hrs., in a 250 cc. graduated flask. It was completely wetted with water by washing several times with distilled water and the flask was filled up to the graduation mark with water whose pH had been adjusted to the required value. As this barium sulphate occupied about 2.8 cc., this volume was subtracted from the total 250 cc. to get the actual volume of solution in the flask. The ferric nitrate solution was prepared and adjusted to the same pH as water by means of dilute nitric acid. The first pH chosen was 2.63, as the ferric nitrate solution was then visibly clear and free from any colloidal ferric hydroxide. 1 cc. of water was removed from the flask and replaced by 1 cc. of ferric nitrate solution containing 0.328 mg. of ferric ion per cc.. The flask was shaken intermittently for about three minutes, the solid allowed to settle for two minutes, and the supernatent solution then tested for ferric ion concentration by pipetting out a known volume and analysing colorimetrically as described above. The volume of ferric nitrate solution added was increased each time and the solution

taken out from the flask was replaced by adding distilled water, where necessary, in addition to the fresh ferric nitrate solution to keep the volume of liquid in the flask constant. The volume removed for analysis was decreased each time to compensate for the increasing concentration of ferric ions in solution.

A second series of adsorption tests was conducted with barytes that had been filmed with a collector coating of laurate. The weighed barytes was allowed to stand in contact for two hours with 0.009 gm. per litre solution of sodium laurate (equivalent to 0.1 lb./ton) which had given 100 per cent. recovery in flotation tests. The soap solution was decanted off and the barytes was washed with distilled water. Subsequent adsorption tests were as described above. In the course of flotation tests with the Hallimond tube, it has been shown that the collector coating on barytes was so firmly held that it could not be removed by simply washing with water four or five times.

The experiments were repeated for a pH value of 4.78. Here a great deal of colloidal ferric hydroxide was found to be present in the solution. It was, therefore, shaken before adding to the flask so as to obtain a homogeneous dispersion of the precipitate. No deposition of this precipitate on the solid was observed.

The cumulative adsorption of ferric ion in mg. per gm. of barytes was plotted against equilibrium concentration in mg. per litre as shown in Figs. (50) to (52). All the

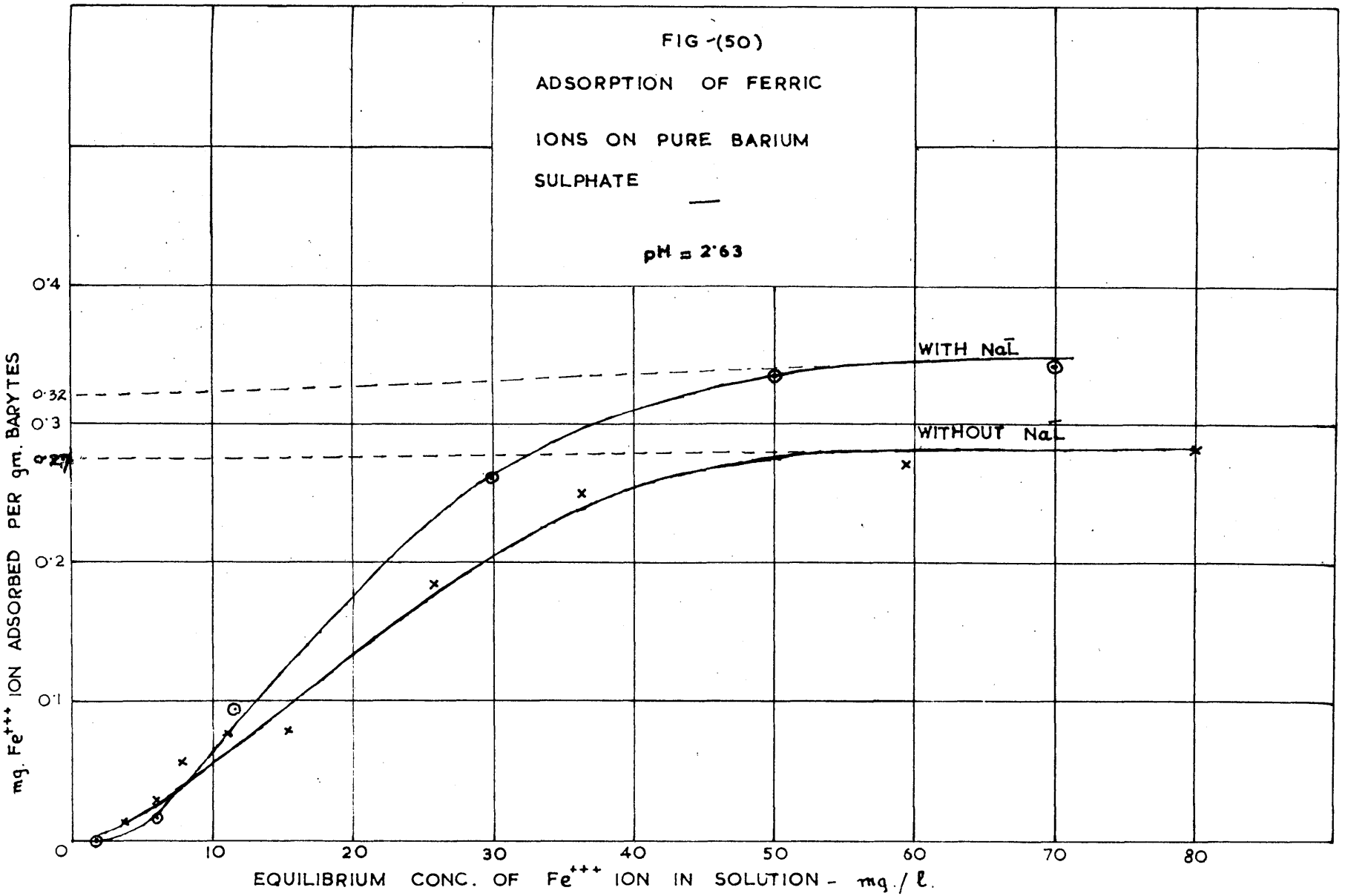


FIG -(50)
ADSORPTION OF FERRIC
IONS ON PURE BARIUM
SULPHATE
pH = 2·63
WITH NaI
WITHOUT NaI
mg. Fe+++ ION ADSORBED PER gm. BARYTES
EQUILIBRIUM CONC. OF Fe+++ ION IN SOLUTION - mg./l.
0·4
0·32
0·3
0·2
0·1
0
10
20
30
40
50
60
70
80

FIG-(51)

ADSORPTION OF FERRIC IONS ON PURE BARIUM SULPHATE

pH = 4·78

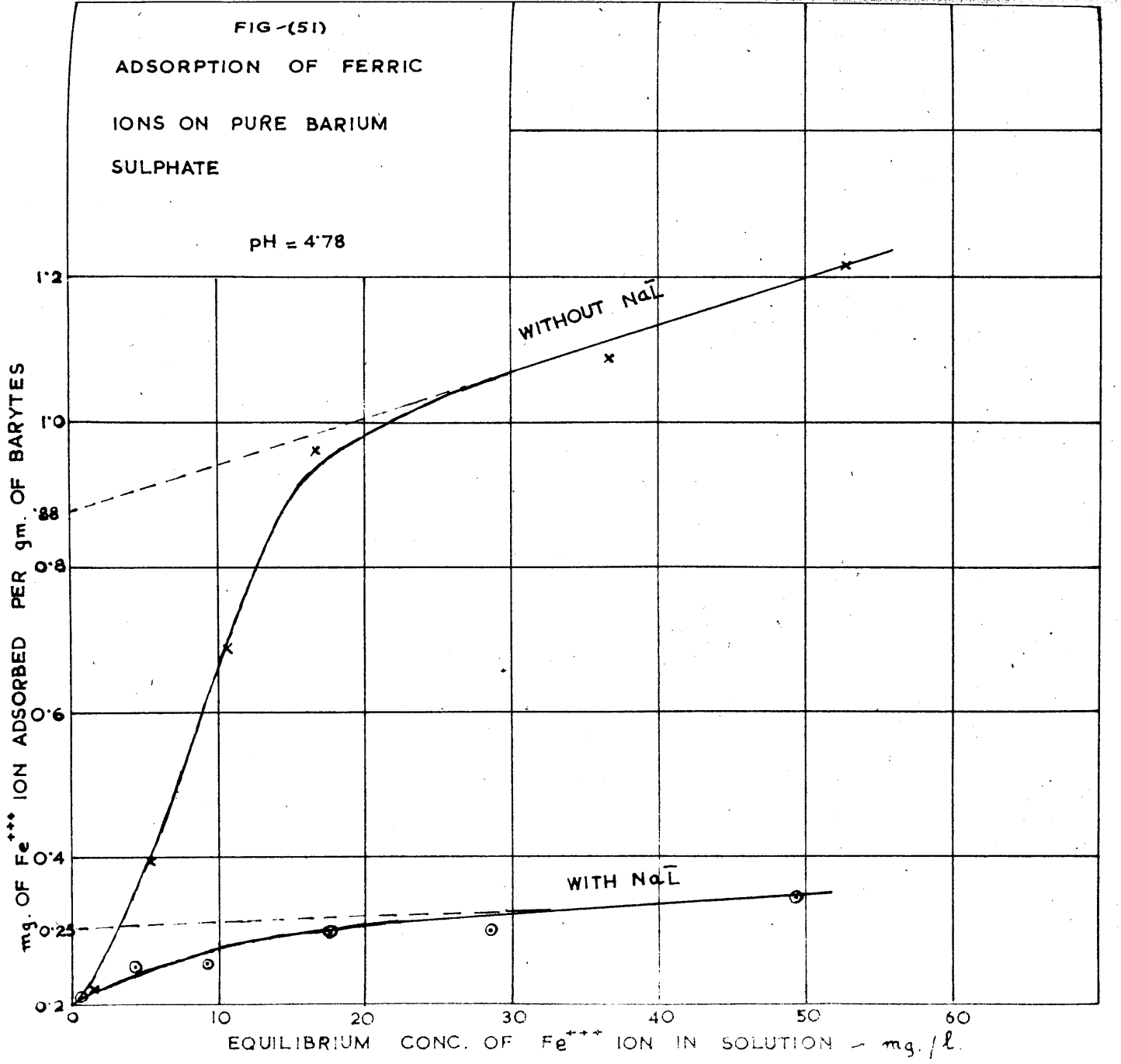
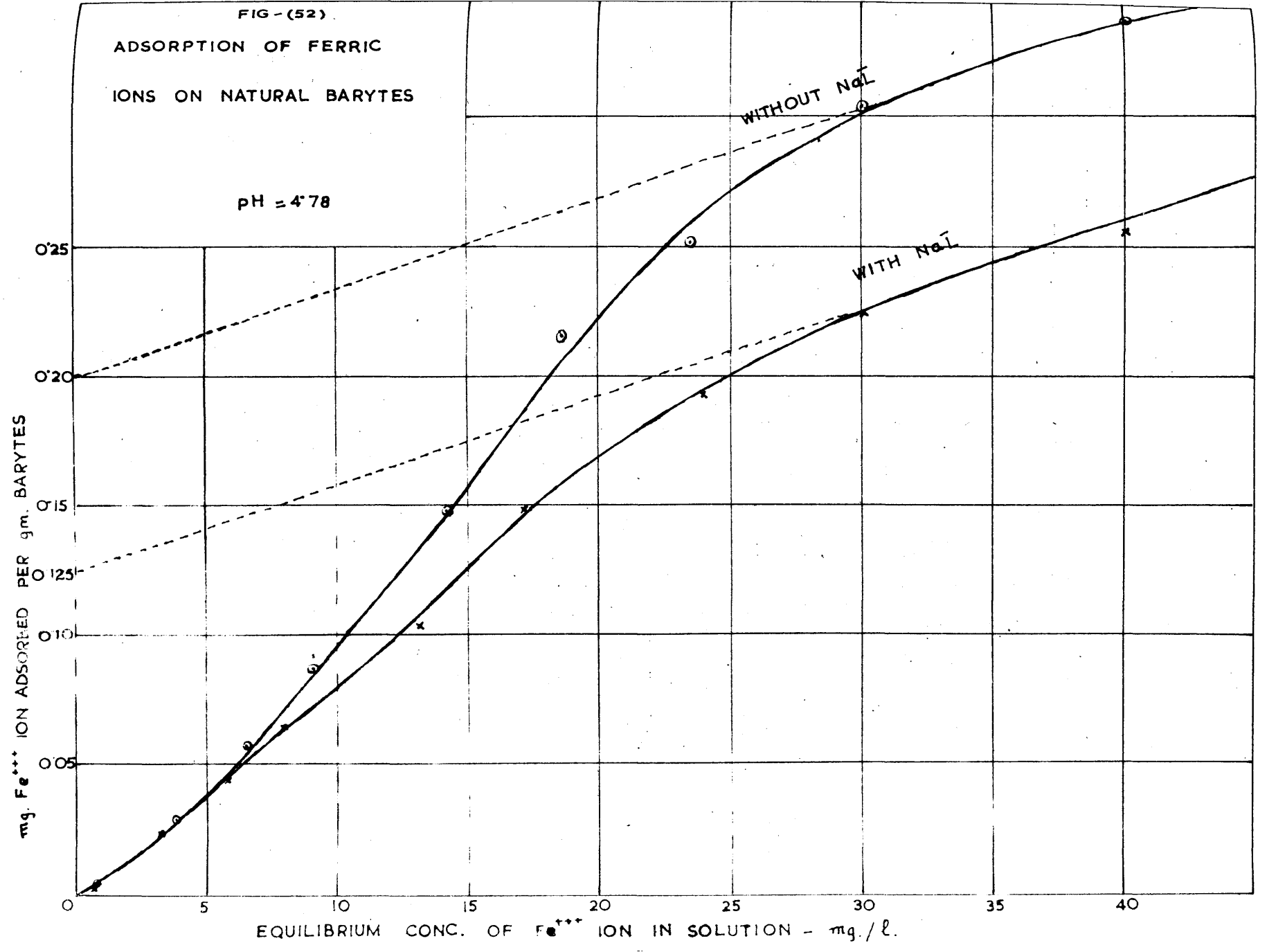


FIG - (52)

ADSORPTION OF FERRIC IONS ON NATURAL BARYTES

pH = 4·78



curves follow the normal trend of isotherms for adsorption at solid-liquid interface, rapidly rising at low concentrations and very slowly at concentrations above the point at which the solid surface becomes saturated with the adsorbed layer. Extrapolation of the upper part of the curves in the normal way gave the adsorption for a monomolecular layer. The maximum adsorption values are given in the following table.

TABLE (12)

Barytes	pH	Maximum Adsorption. mg. Fe^{+++} gm. of barytes	
		With $NaL\bar{a}$	Without $NaL\bar{a}$
Pure $BaSO_4$	4.78	0.25	0.88
	2.63	0.32	0.27
Natural (130-300 mesh)	4.78	0.125	0.20

Now, the specific surfaces of the natural and synthetic barytes, as determined by the Lea and Nurse method, are 542 and 138.5 $cm.^2$ per gm. respectively. On converting these to the gas adsorption values, by multiplying with the factor 1.9, 1029.8 and 263.1 $cm.^2$ per gm. respectively are obtained. Then, taking the ionic radius of ferric ion as 0.67 Å, and using these surface area values, the quantities of ferric ion necessary for unimolecular layer formation were calculated to be 0.678 mg. per

gm. barytes for the natural barytes and 0.116 mg. per gm. barytes for pure barium sulphate.

The adsorption results for pure barium sulphate, in Table (12), at pH 4.78, indicate the formation of an unimolecular layer in the presence of laurate collector coating and of a multimolecular layer of about 8 molecules thick in the absence of collector coating. On the other hand, the adsorption on natural barytes at the same pH (4.78), has not reached the unimolecular stage even without the collector coating although the equilibrium concentration range is almost identical with that for pure barium sulphate. In this connection, it should be noted that the surface of the latter is saturated at an equilibrium concentration of about 20 to 40 mg. of ferric ions per litre.

As mentioned previously, because of the non-porous character of barytes crystals, their absolute surface areas would not be far different from the above experimental values. Consequently, multimolecular adsorption is plausible and in line with the strong affinity of iron for barytes.

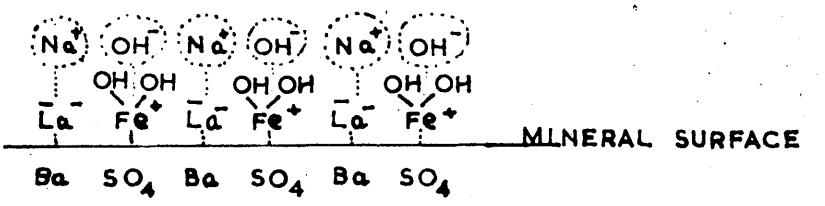
A likely error in the above tests was the adsorption on the glass walls of the graduated flask. A blank experiment without any barytes gave the adsorption by the glass walls as 0.01 mg. of ferric ions at an equilibrium concentration of 58.5 mg. per litre. This is only a negligible fraction of the total adsorption in any of the foregoing cases.

At pH 4.78, both natural and synthetic samples show lower adsorption in the presence of a collector coating.

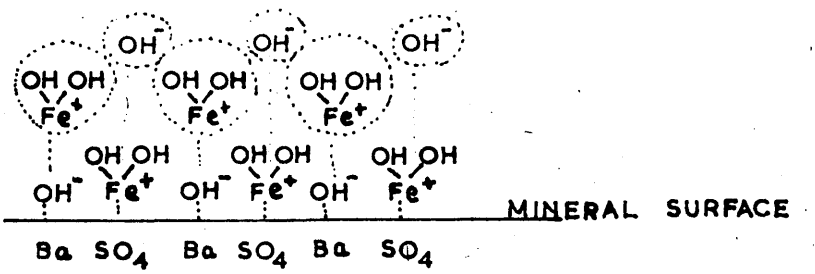
FIG - (53)

ADSORPTION OF FERRIC

IONS ON BARIUM SULPHATE



(a)



(b)

The difference is greater in the case of synthetic barytes probably because the natural mineral has already had some iron compounds in the crystals. This suggests that, where a collector film has first been formed on the surface, ferric ions are adsorbed only at those points not occupied by the collector laurate ions as in Fig. (53a). When, however, no collector film is present, ferric ions are adsorbed on the entire surface as shown in Fig. (53b).

The hydrogen and hydroxyl ions are supposed to be adsorbed initially on the surface of barytes when water alone is present. Laurate ions are adsorbed by exchange with the hydroxyl ions while the ferric ions are adsorbed by exchange between the hydrogen ions and $Fe.(OH)_2^+$ ions. When, however, no laurate ions are present on the surface, further adsorption of ferric ions takes place this time opposite the barium atoms, forming counter ions to the already adsorbed hydroxyl ions in the compact double layer as shown in Fig. (53). Multilayers of ferric ions may have formed through the action of van der Waal's forces, the effective distance of which is still undecided.

However, at pH 2.63 the adsorption with laurate ion coating appears to be a little higher than that without it. The difference may only be accidental and it is thought that it is due to the difference in surface areas of the two different samples used. The results, therefore, indicate no real change in adsorption of iron due to collector coating in this particular case. The non-agreement between this and the

results at pH 4.78 is attributed to the low pH. The high acidity of this solution will reduce the possibility of the presence of iron hydroxides or other basic substances and will tend to change the collector coating to that of undissociated lauric acid. Ferric ions are thus probably absorbed as such instead of as hydroxides as in the previous case. This adsorption is not affected by the presence of a collector coating.

The above hypothesis on the mode of adsorption of ferric ion barytes points to the facts:-

1) ... That ferric hydroxide is involved in the adsorption.

2) ... That because of the adsorption of ferric ions on the surface with OH^- ions oriented outwards, the surface is made hydrophilic to the extent to which this adsorption has taken place. Consequently, the wettability of the particles increases with iron adsorption and the chance of mineral-bubble attachement is thus reduced.

An alternative explanation for the action of ferric ions can be given on the basis of the work done by Taylor and Bull (72). The cations, especially those of multivalent heavy metals, have been known to possess a powerful depressant action on the flotation of many minerals. From their investigations on the effect of several cations, such as Ag^+, Cd^{++}, Co^{+++}, on the flotation of galena, they suggested that these cations are strongly adsorbed, thereby giving to each particle of mineral a strong positive charge. The particles would then repel one another so strongly that only a limited number could attach

themselves to each air bubble.

Now, substances, precipitated from solutions, generally tend to adsorb either their own anion or the cation depending on which are in excess in solution. For example, barium sulphate adsorbs sulphate ions when precipitated with sulphurate ions in excess and barium ions when the latter are in excess. Similarly with silver iodide, it may be either the silver ions or the iodide ions that are adsorbed. The colloidal precipitates are usually charged in this way.

Ferric hydroxide has been obtained both positively and negatively charged by F. Powis (73). Ferric chloride and caustic soda gives the colloidal precipitates, $(Fe_2O_3 . x\ H_2O)\ Fe^{+++} : 3Cl^-$; $(Fe_2O_3\ x\ H_2O)\ OH^- : Na^+$. The former was given in excess ferric chloride solution and the latter in excess caustic soda. If the ferric hydroxide produced at pH 4.78 were thus electrically charged, and if the adsorption had taken place in this form, it would be reasonable to apply Taylor and Bulls' suggestion to this case too.

.....

SURFACE AREA OF POWDERS.

Chapter IX.

For the past 25 years it has been generally accepted that the adsorption of collectors on the surface of the mineral particles is responsible for the flotation process. The ability of solids to adsorb foreign substances from gaseous and liquid media, the contact angle measurements in solutions, and the proved abstraction of collectors from solutions in flotation experiments, are all in direct support of this belief. Consequently, studies of solid surfaces expecially those of the minerals, have become of importance for the elucidation of flotation theory. Thus it is that new methods of determining surface areas of mineral particles are being continually sought.

So far no definite conclusions have been arrived at as to whether it is necessary for the mineral surface to be wholly covered with a monomolecular layer of the collector before a hundred per cent recovery is achieved. The two main obstacles to the solution of this problem are the lack of a method of surface area determination sufficiently quick but accurate, and also the difficulty of measuring adsorption at solid-liquid interface.

Although a variety of methods are now available for the measurement of surface area of solids, none of them can be put to a general use. Each has its own advantages and

and disadvantages and the scope of each method is restricted, as for example, while very fine particles cannot be used in the permeability method the quantity of material needed in the gas adsorption method is limited by the affinity it has for the gas to be adsorbed and by its fineness.

The three methods considered by the author are the liquid or air permeability, the gas adsorption and the size analysis methods. Cooke and Digre (74) employed the permeability method of Kwong (75) in their studies on the activation of quartz with calcium ions. They checked their results by size analysis, applying Gross and Zimmerleys' (76) shape correction factors. Kraeber and Boppel (43) made use of the size analysis followed by a calculation of surface area by means of Gross and Zimmerleys' shape factors, in their work on the action of metallic salts on flotation of non-sulphide minerals. A similar procedure was adopted by Gaudin and Rizo-Patron (77) in their investigation on the activation of quartz by barium ions. Then the gas adsorption method or the B.E.T. method was applied by Gaudin and Preller (58) in their attempt to find a relationship between the surface area and the quantity of collector required in the flotation of sulphide minerals.

The objects of the surface area determination in this thesis are,

(a) to find out the extent to which adsorption of lower fatty acids takes place on the mineral surfaces.

(b) to see if any relation exists between the

flotation of barytes with fatty acids and their soaps and the surface area of barytes.

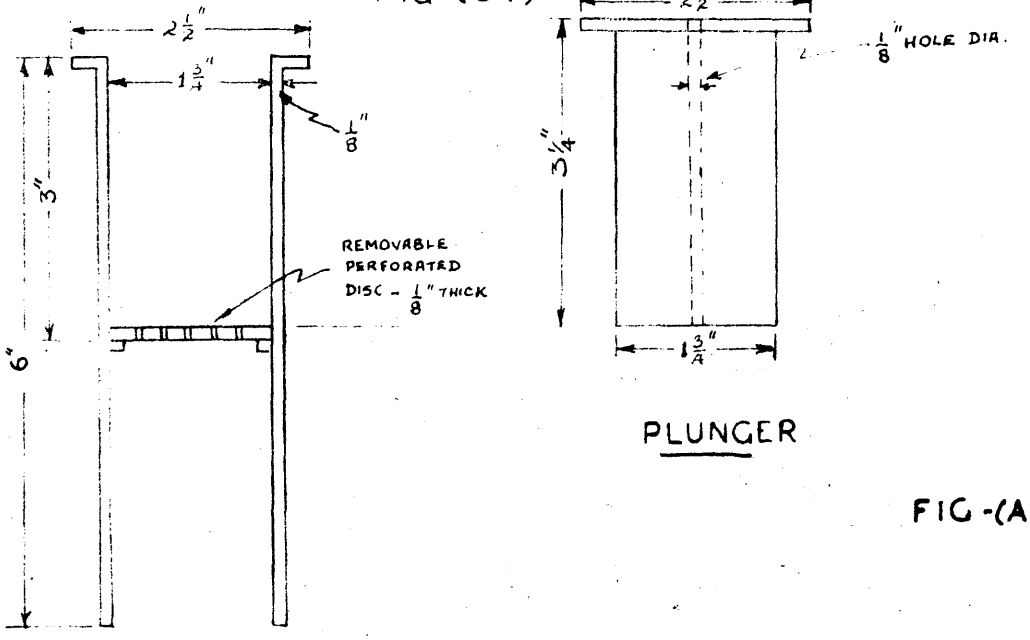
and (c) to determine the role of the surface area in the activation and depression of barytes with metallic ions.

An absolute method, capable of giving the true surface area, is actually required in such investigations of fundamental nature but the known "absolute" method, making use of the calorimetric procedure, by Harkins and Jura (78) is too tedious for routine determinations. Another absolute method (79) by the same authors relates the results obtained by the B.E.T. (80) methods to those obtained calorimetrically. Though this reduces the amount of labour, the B.E.T. method itself is time consuming and so it was decided to employ the simpler and quicker permeability method. As the present work deals, in most cases, with relative results this method should serve the purpose well. Moreover, surface areas so obtained could be converted to those of the gas adsorption method by applying the ratio of the surfaces given by these two methods. This corrected value would not be very far from the true surface area as barytes is a relatively non-porous material.

Rigden's Liquid Permeability Method.

The first apparatus to be tried out was that of Rigden (81) shown in Fig. (54 A & B). The permeability tube and the plunger were made of brass and the dimensions are as given in Fig. (54 A). In the original form by Rigden an

FIG-(54)



TUBE

PLUNGER

FIG-(A)

DIMENSIONS OF TUBE & PLUNGER

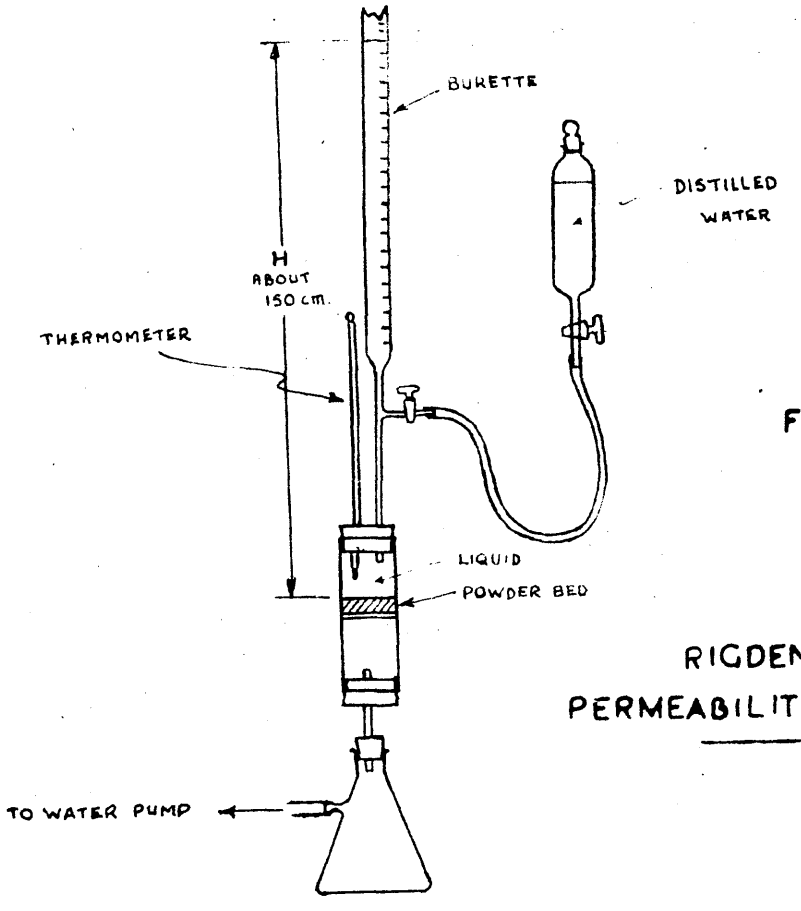


FIG-(B)

RIGDEN'S PERMEABILITY APPARATUS

ordinary cm. scale and a vernier scale were attached to the sides of the tube and the plunger respectively. This was slightly modified in the author's apparatus to enable a more accurate reading to be made of the depth of the powder bed. Eight equally spaced radial markings were made on the flanges of the plunger and of the tube so that, after placing these lines one above the other, the distance between the top of the plunger and lower part of the flange in the tube could be measured at eight different places by means of a micrometer screw gauge. The mean of the readings is taken as the actual distance.

The procedure was as follows. Three filter papers were placed on the perforated disc in the tube and the mean distance between the plunger and the top of the tube taken as described. The tube was then mounted on a Buchner flask connected to a water pump as in Fig. (54 B). After filling it with water a known weight of the powder was gradually dropped into the water. This allowed the powder to be completely wetted and all air in the powder to escape. When the whole of the powder had been added, the top surface of the bed was levelled roughly with a glass spatula. The water level was brought up to the top of the tube, and the water then sucked through the bed for some time producing initial compaction of the bed. In this draining process care was taken to continually replace the water as it drained away. It is important that no air gets into the bed. Another circle of filter paper was placed on top of the powder bed

and gently pressed down. Having disconnected the tube from the flask and inserted the plunger, surplus water being expelled through the central hole, the plunger was tightly pressed down and further compaction of the bed achieved by tapping the tube and plunger smartly on the bench about four or five times. The average distance between the top of the tube and the plunger was again taken as described. The difference between this and the previous reading gives the height of the bed. The tube was then put back in position over the flask, the plunger gently removed with a rotary motion and the top of the tube immediately filled with water. Water was sucked through for about 10 minutes maintaining the water level always above the powder bed as before. This procedure removes any traces of air that might have entered the bed during the compaction process.

Taking special care that the water was up to the brim of the tube, the rubber bung, fitted with the burette and the thermometer, was pushed gradually into the tube. The water level in the burette was then allowed to fall driving the water through the bed and was timed over a measured volume. The mean height of the water level above the centre of the bed was measured during the test. The mean temperature of the water in the tube was noted and the values of the viscosity and density of water at this temperature were obtained from the International Critical Tables.

The specific surface of the solid is calculated from the following equation:-

TABLE (13)

Surface Areas of Minerals by

Rigden's Liquid Permeability Method.

Mineral	B.S.S. Mesh Size	Porosity	Sp. Surface $cm^2/gm.$
Silica	50-60	0.237	200.2
	under 160	0.247	1051
Barytes	120-150	0.306	314.1
		0.264	328.9
	130-300	0.371	750.4
	under 150	0.281	1526
			1524
		0.331	1385
			1377
		0.335	1663
			1634
		0.343	1281
			1287
		0.373	1917
			1906
		0.446	1526
			1327
Pyrites	under 150	0.359	2928
			2551
		0.360	3445
			3615
		0.374	3332
			3365
		0.382	3844
			3763
		0.383	4467
			4478

$$\text{Specific surface, } S_L = \sqrt{\frac{A \sigma g H \varepsilon^3}{5 \eta \rho^2 Lv(1-\varepsilon)^2}}$$

where A = cross-sectional area of the permeability tube, ($cm.^2$)

H = mean head of liquid over the bed, (cm.),

η = liquid viscosity in poises,

σ = liquid density in gms. per cc.

L = depth of bed in cms.

v = volume rate of flow through the bed in cc. per sec.

ρ = density of solid in gms. per cc.

Discussion.

Surface areas of three minerals as determined by this method are given in Table (13). Two or three values, given for one porosity, were obtained by varying the mean height of the water level over the bed from about 10 to 20 cms.. Except for the samples of barytes at porosity 0.446 and pyrites at 0.359, the close agreement between the figures in each set indicates that the mean height of water level, when not varied to a great extent, has little or no effect on the surface area calculation. Rigden estimated the standard deviation of the mean S_L values to vary from $\pm$ 1.2 % to 5.0%.

The standard deviations calculated from the figures in Table (13) are:-

Barytes under 150 mesh:-	porosity up to 0.373-	8.92%
	surface area	14.0%
Pyrites under 150 mesh:-	porosity	2.8%
	surface area	15.4%

These are much higher than Rigden's estimated values. It must, however, be considered that the measurements were done on different samples taken from the same lot of ground ore and it is not impossible to have a wide variation in surface area of these samples. Furthermore, unless by coincidence, it is not possible to reproduce the same porosity a number of times and there seems to be no definite relation between the surface area and porosity.

An unusual phenomenon, not described by Rigden, was observed in the determinations. The time required for a certain fixed volume of water to flow through the bed falls as the experiment is repeated even though the mean height of water level is kept constant. The two probable causes are the further compaction of the bed and the rearrangement of particles in the bed tending to obstruct the flow of water. Since the bed has already been compressed to the minimum depth, the latter reason is the more likely of the two.

Two precautions are necessary while carrying out a measurement:-

1) ... The filter paper on top of the bed tends to be punctured by the central hole in the plunger when the latter is pressed down in the tube. As the plunger itself is quite heavy a pressure sufficiently high to burst the filter paper should not be applied.

2) ... The prepared bed is liable to be displaced up the tube on removing the plunger in spite of the great care exercised in so doing. An absolutely gentle rotary motion of the

plunger is essential if the bed is not to be disturbed.

Apart from the above criticisms, it can only be said that the method is simple to operate and is quite suitable for non-porous materials like barytes and silica as is later shown by the comparison with the gas adsorption results.

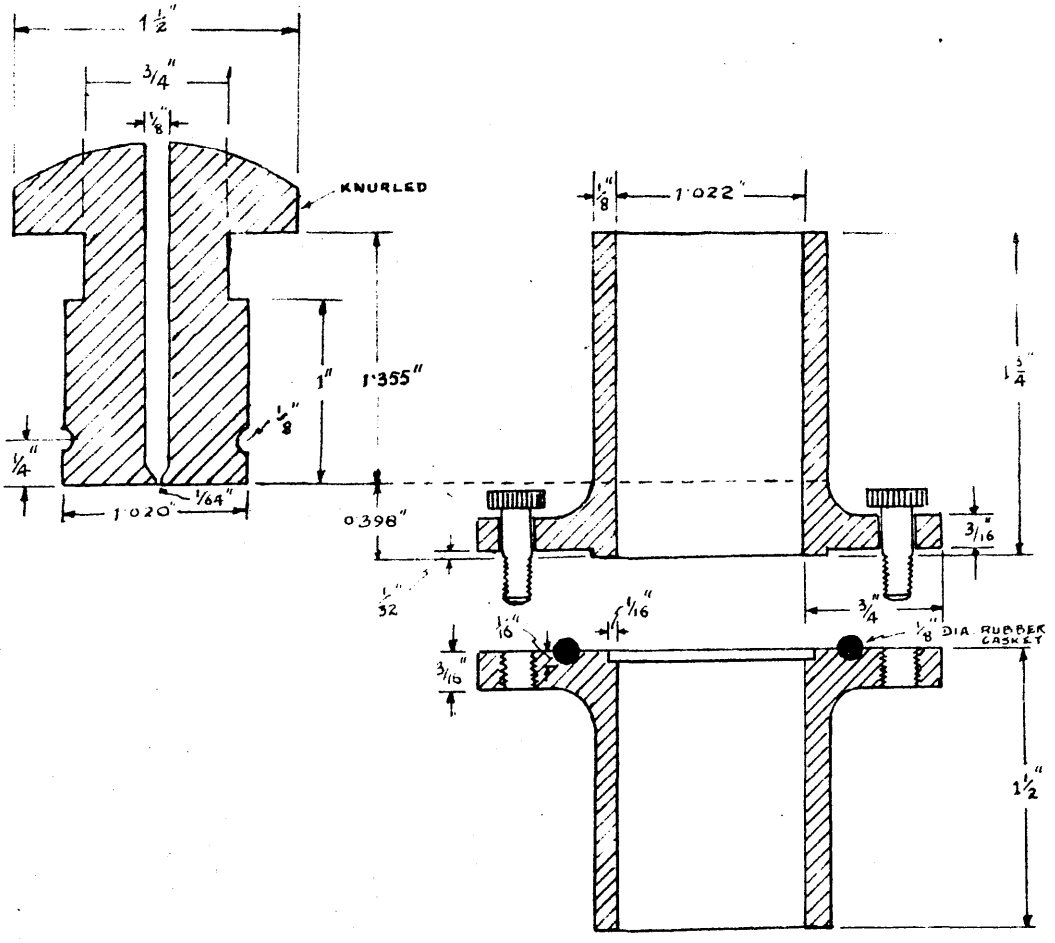
Lea and Nurse Air Permeability Apparatus.

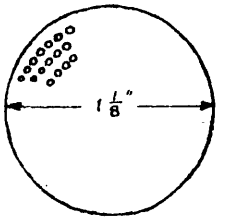
The chief objection to the use of Rigden's method is that it requires not less than 20 gms. of barytes for each determination. As only 15 gms. of the ground ore is taken for a flotation test, a method which needs less than this quantity was required. This was found in the Lea and Nurse Apparatus (82) which can be operated with only 12 to 13 gms. of barytes at a porosity of about 0.475.

The details of the permeability cell are shown in Fig. (55) and the layout of the apparatus is as sketched in Fig. (56). The small deviations in the dimensions of the depth of the bed and the cross-section of the cell from the actual required values are due to faults in workmanship and appropriate corrections are, therefore, made in the surface area calculations.

The general procedure is as described in British Standard Specifications (83). The flowmeter was calibrated by passing air through the capillary tube and collecting the water displaced over a known length of time. The flowmeter constant C was calculated as follows:-

FIG - (55)



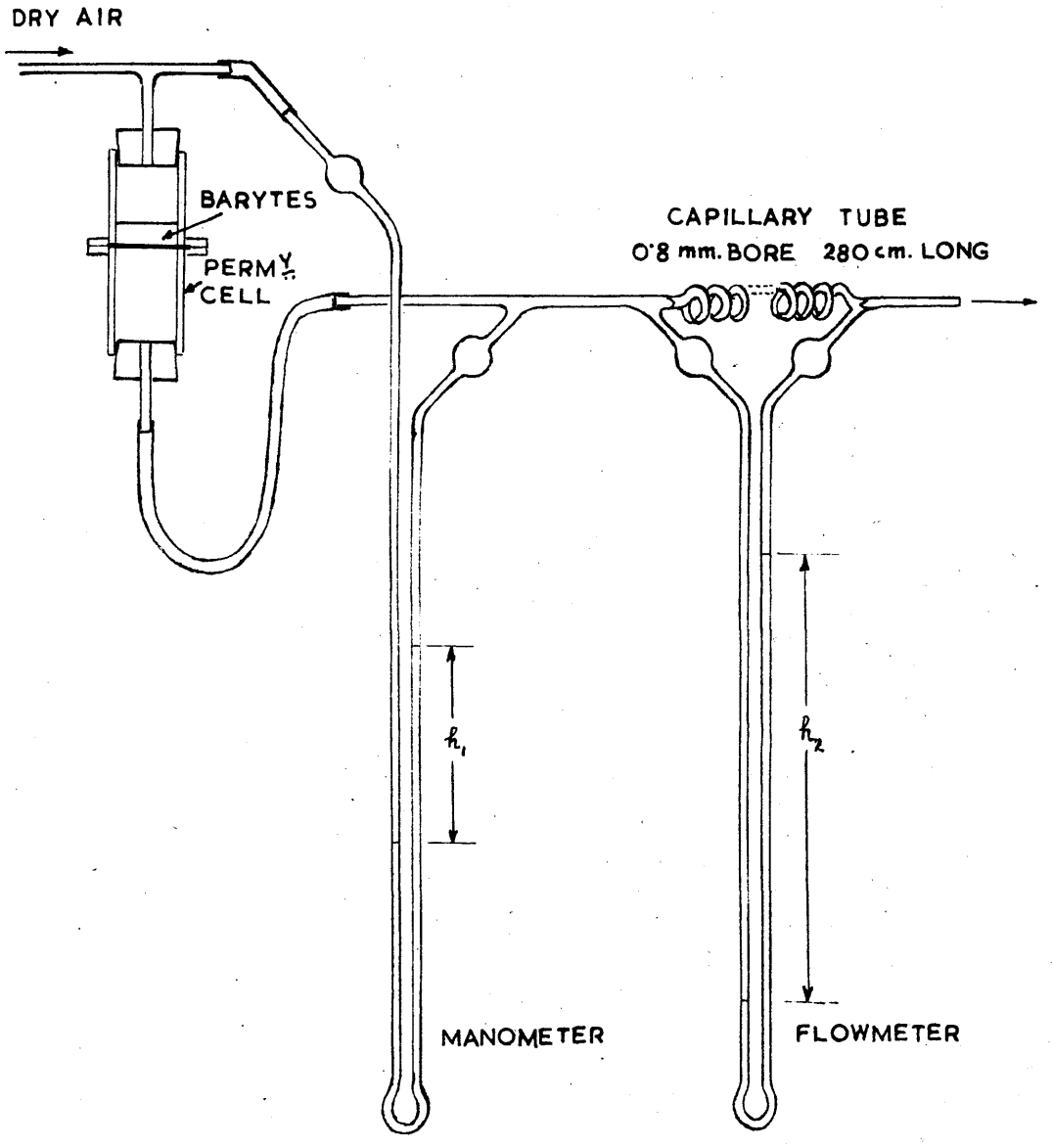


PERFORATED PLATE 1/16" THICK 1/16" HOLES, SPACED 3/32"

SCALE_ FULL SIZE

DETAILS OF PERMEABILITY CELL

FIG - (56)



LEA & NURSE
AIR-PERMEABILITY APPARATUS

Average C = $\frac{Qn}{h_2 d_L}$ where Q = volume of dry air in cc. per sec. corrected to atmospheric pressure.

n = viscosity of air at the given temperature in C.G.S. units.

h_2 = flowmeter reading in cm.

d_L = density of kerosene in flowmeter.

$Q = \frac{V}{t} \cdot \frac{(P-p)}{P}$ where V = measured volume of air in cc.

P = atmospheric pressure.

p = vapour pressure of water at room temperature.

t = time of collection of air in secs.

The average C was found to be 3.951×10^{-6} C.G.S. units which is within the specified value of 2.0 to 4.0×10^{-6} units.

Air-tightness.

After raising the pressure to 12 cms. of kerosene as read on the manometer, the air inlet and outlet were sealed tightly by means of screw-clips. The fall in the manometer reading was recorded as 0.024 cm./min. which is lower than the allowable drop of 0.05 cm./min.

Density of Barytes.

The true density of barytes was determined by the

specific gravity bottle method using kerosene as the liquid. The effect of temperature variation on the densities of barytes and kerosene are given in the following table.

TABLE (14)

Temperature °C	Density of Barytes.	Sp. gravity of Kerosene.
15	4.428 gm./cc	0.779
17	4.434 " "	0.778
20	4.455 " "	0.774
22	4.474 " "	0.773
25	4.490 " "	0.774

From the above table, it can be seen that the percentage change in density of barytes is practically double that of the specific gravity of kerosene in opposite directions. This is a strange behaviour which is hard to explain. Dunbar (84) also obtained similar results when working with dolomite. In that temperature range where the room temperature generally lies, the variations are, however, comparatively small, being in the second and third decimal places only. The density at 20°C, i.e. 4.455 gms./cc., was used in all calculations as the room temperature was always near 20°C at the time when the apparatus was being used.

Procedure.

12.48 gms. of dried barytes, to form a bed of porosity 0.475, was added to the permeability cell and the surface was levelled off by gently shaking the cell followed by allowing it to fall four times on a wooden bench from a height of about 1 cm.. The plunger was next inserted slowly and pushed home so that it sat exactly on top of the cell, and was then removed by a gentle twisting motion. The upper rubber bung was fitted in position and the air admitted slowly to the cell. The rate of air flow was adjusted until the flowmeter recorded a difference in levels of 30 to 50 cms. Readings of manometer, h_1, were taken at various rates of air flow, h_2, and the surface area then calculated from the equation:-

$$S_w = \frac{14}{d(1-\varepsilon)} \sqrt{\frac{\varepsilon^3 A}{CL} \cdot \frac{h_1}{h_2}}$$

where, ε = porosity of powder bed = 0.475

A = cross-section of cell = 5.29 cm^2.

L = height of bed = 1.011 cm..

d = density of barytes = 4.455 g./cc.

C = flowmeter constant = 3.91×10^{-6} C.G.S. units.

Discussion of Results.

The surface areas of three different mesh sizes of barytes, as determined by the Lea and Nurse method, using only one porosity value, are given in the following Table.

TABLE (15)

B.S.S. mesh size.	porosity	Specific surface $cm.^2/gm.$
120-150	0.475	485.5
		485.0
130-300	"	541.1
		543.8
		540.5
		548.4
		540.7
under 300	"	1635.0
		1614.0

The maximum deviation from the mean, in these values, is 5%, indicating that this method would serve very well for comparative purposes. As the main object here was to achieve reproducible surface areas as near to the true values as possible, the change in specific surface with other variables such as porosity and particle size was not investigated. Since one determination takes only about 15 minutes, it is much quicker than the Rigden's apparatus.

Gas Adsorption Method.

The two methods described above give only the

external surface area. As the present paper is concerned with adsorption at the surfaces of powders, it is desirable to know the internal surface as well. Owing to the fact that barytes is a non-porous substance, its internal surface will be relatively small compared to that of the external. That this is so was confirmed by the results from the gas adsorption method which was employed to obtain a correction factor to be applied to the figures from the permeability methods.

The adsorption apparatus, shown in Fig. (57), was the same as that used by Macmillan (85). It consists essentially of a bulb containing about 10 cc. of the adsorbent to be tested and connected to the following units:-

(i) An apiezon oil manometer,

(ii) the vacuum pumps and a Piranni gauge,

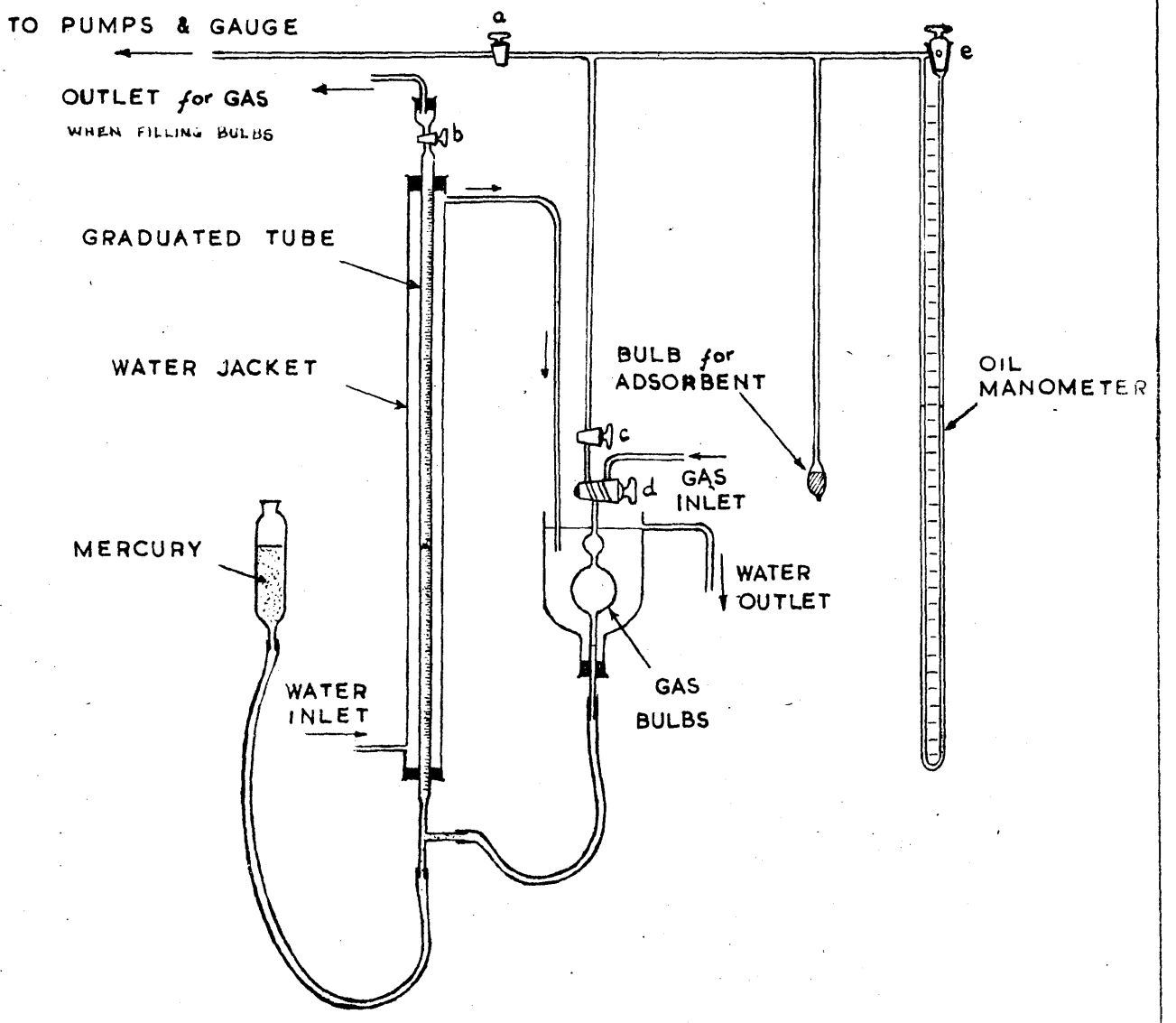
and (iii) a gas storage bulb and a burette filled with mercury.

The oil manometer records the gas pressure in the adsorption system when the stop-cock (e) is closed maintaining a vacuum in the right limb of the U-tube.

For the evacuation of the bulb, a rotary vacuum pump is backed by a mercury vapour pump and the pressure is read on a Piranni gauge.

The gas for adsorption is stored in a bulb surrouned by a water jacket. There are two calibration marks on the stem of the bulb; the lower mark was used for filling with nitrogen or nitrous oxide gas while the upper one was for helium.

FIG- (57)



GAS ADSORPTION APPARATUS

The two way stop-cock (d) provides an inlet for the adsorbate and the bottom of the bulb is connected to a burette and a mercury reservoir. The burette, water jacketed, is graduated over 20 inches with 1000 equal divisions. It gives the pressure of the gas in the bulb which is proportional to the quantity of gas when the volume is constant.

The procedure was first to open the stop-cock (e) to the vacuum line and with (d) closed, the rotary vacuum pump being started after opening (a) and (c). When the pressure had fallen below 10^{-2} mm. Hg as indicated by the gauge, further reduction in pressure to less than 10^{-4} mm. Hg was achieved by the help of the mercury vapour pump. To remove affectively any adsorbed gases or vapours from the powder, the evacuation was continued over a period of about an hour while the bulb was heated to a temperature of 450-500°C in a molten metal bath. The bulb was then allowed to cool down to room temperature keeping the vacuum pumps in operation to ensure that the surface was perfectly clean.

Prior to the admission of gas into contact with the solid, the stop-cock (c) was closed and the two-way stop-cock (d) was opened to the gas inlet. The mercury reservoir was lowered to let the pure nitrogen gas pass through the bulb and the burette. The rate of flow of gas was observed by bubbling it through water at the outlet. A fairly fast rate of flow was maintained for about 10 minutes in order to make sure that all air had been swept away from the system. Slowing down the gas flow, the mercury level was raised further to a little

above the stop-cock (b). The latter was closed and the mercury level lowered and raised again thus driving off all gas bubbles trapped between the mercury and the wall of the burette. In this manner a vacuum was obtained when the mercury level was brought down with (b) closed.

For actual gas adsorption measurement, the stop-cock (a) leading to the vacuum line was closed and the bulb containing the adsorbent was immersed in a thermos flask filled with liquid air at -190°C. The zero reading of the burette was taken by placing the mercury meniscus at the lower calibration mark. Small additions of nitrogen gas was made into the adsorption system by opening (d) toward (c), then closing it and opening (c). The stop-cock (e) was, of course, closed before this so that the space over the oil in the right limb of the U-tube is preserved under vacuum. At each admission the readings of the burette, the manometer and the thermometer of the circulating water were taken. The calibration of dead space with helium was carried out in the same way except that it was usually done before nitrogen adsorption as this precluded any necessity to desorb nitrogen from the solid surface.

For the determination with nitrous oxide, the adsorbed nitrogen was removed by evacuation as described and the above cycle of operations repeated. Nitrous oxide gas was introduced this time instead of nitrogen.

In surface area calculation the volume of gas admitted at N.T.P. was obtained from the equation:-

TABLE (16)

Specimen Experimental Readings

Gas	Water Bath Temp. °C.	Burette Reading	Manometer Reading cms. oil
Helium	24.3	723	0.00
	24.3	693	1.10
	24.2	668.5	3.00
	24.0	646	4.80
	23.9	612	6.55
	23.8	579	8.30
	23.8	550	9.70
	23.8	491	12.95
Nitrogen	25.5	927	0.00
	25.4	905	0.00
	25.1	882.5	0.15
	25.0	856	2.65
	25.0	835	5.30
	24.6	809	9.20
	24.2	784.5	12.45
	23.5	759	15.95
	23.3	725	21.15
	23.3	693	26.00

TABLE (17)

Volumes of Nitrogen Adsorbed Calculated From Results in Table (16)

Pressure cms.-oil	Vol. of Gas cc.N.T.P.	Vol. Admitted cc.	Dead Space Vol.-cc.	Volume Adsorbed ccs.
0.00	4.38	0.00	0.00	0.00
0.00	4.29	0.09	0.00	0.09
0.15	4.17	0.21	0.048	0.162
2.65	4.06	0.32	0.08	0.24
5.30	3.96	0.42	0.16	0.26
9.20	3.85	0.53	0.275	0.255
12.45	3.73	0.65	0.37	0.28
15.95	3.62	0.76	0.47	0.29
21.15	3.47	0.91	0.62	0.29
26.00	3.32	1.06	0.762	0.298

TABLE (18)

Comparison of Specific Surfaces by Rigden's and Gas Adsorption Methods.

Mesh Size	Specific Surface- $cm^2/gm.$ Rigden's	N_2-Adsorption	N_2O- Adspt.	Ratio (In Order)
Under 150 (1)	832.5	999.3	669.7	1.52:1.80:1
120-150 (2)	314.1	382.0	210.1	1.50:1.82:1
120-150 (3)	328.9	398.0	225.3	1.46:1.78:1

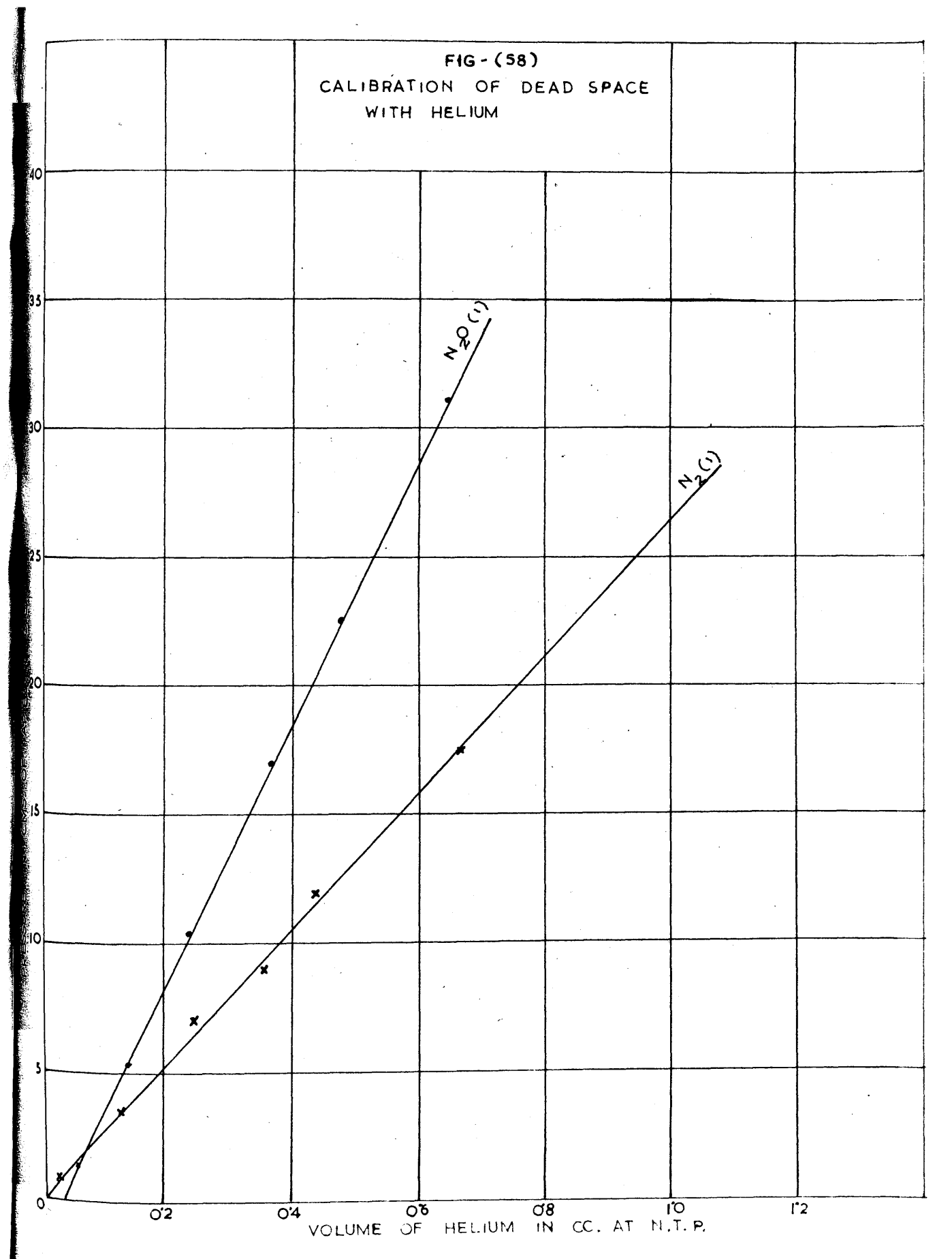


FIG - (58)
CALIBRATION OF DEAD SPACE
WITH HELIUM
40
35
30
25
20
15
10
5
0
N_2O (l)
N_2 (l)
0·2
0·4
0·6
0·8
1·0
1·2
VOLUME OF HELIUM IN CC. AT N.T.P.

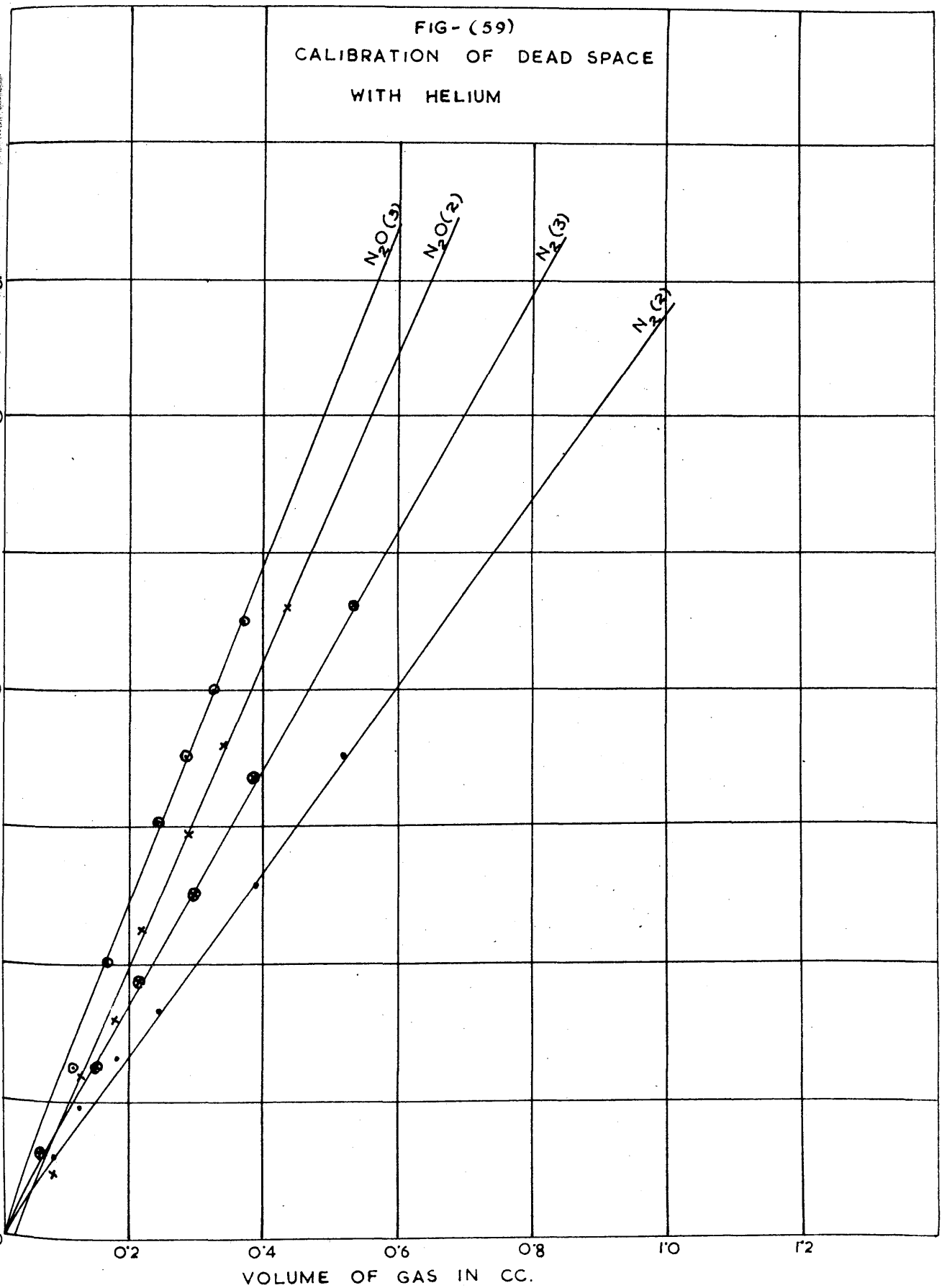


FIG- (59)
CALIBRATION OF DEAD SPACE
WITH HELIUM
N_2O(3)
N_2O(2)
N_2(3)
N_2(2)
0
5
10
15
20
25
0·2
0·4
0·6
0·8
1·0
1·2
VOLUME OF GAS IN CC.

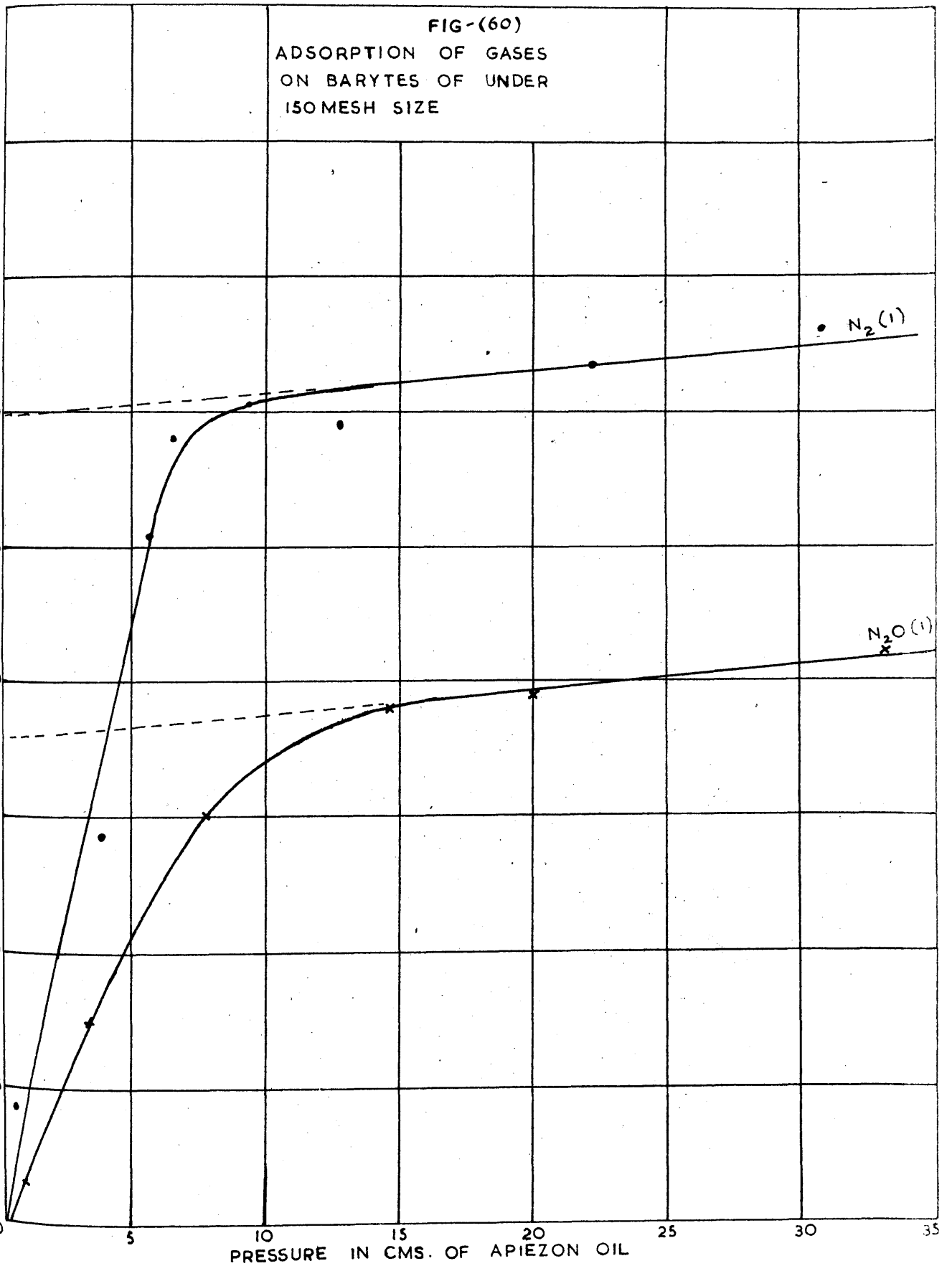


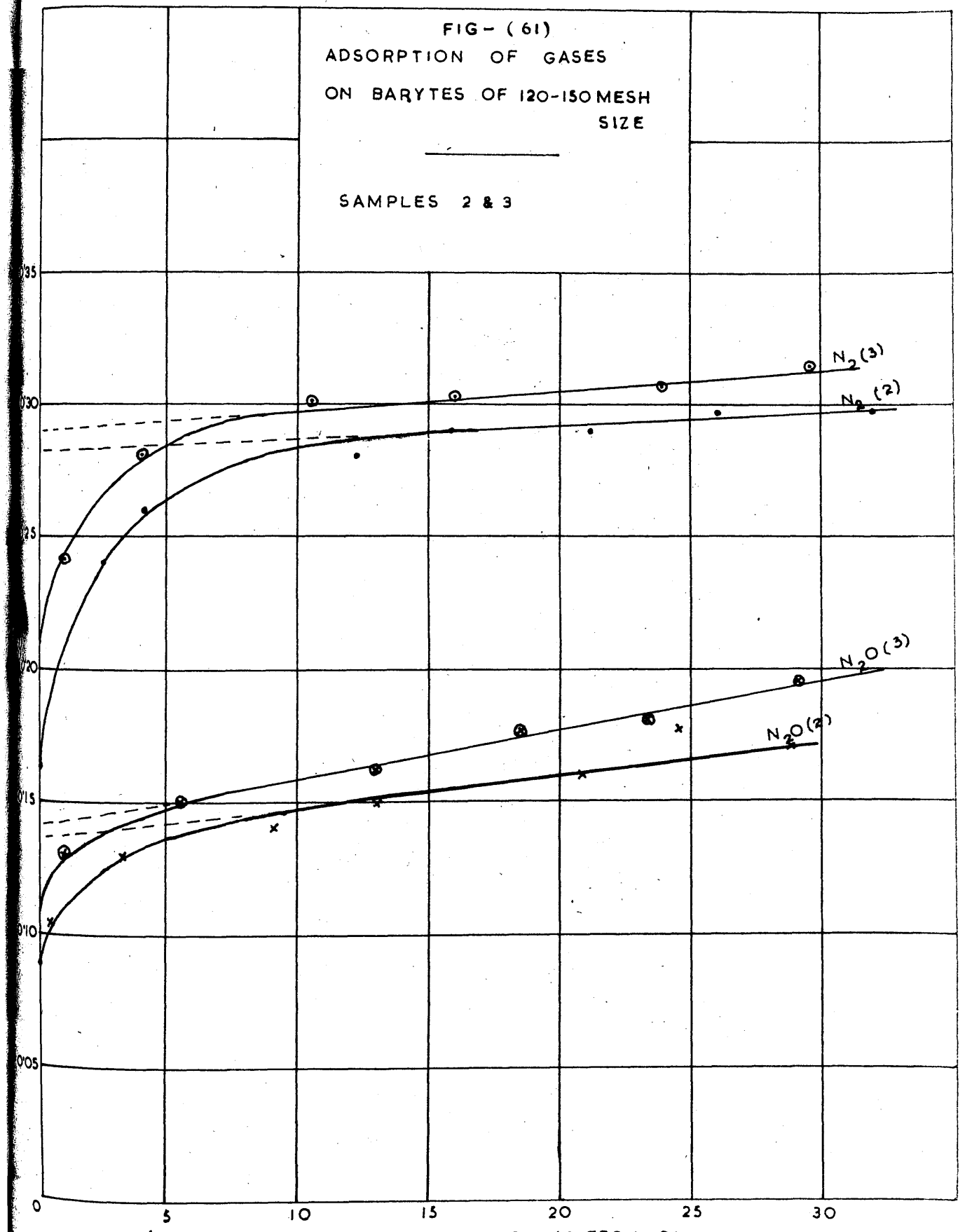
FIG-(60)
ADSORPTION OF GASES
ON BARYTES OF UNDER
150 MESH SIZE
0·35
0·30
0·25
0·20
0·15
0·10
0·05
0
5
10
15
20
25
30
35
N_2 (l)
N_2O (l)
PRESSURE IN CMS. OF APIEZON OIL

FIG- (61)

ADSORPTION OF GASES

ON BARYTES OF 120-150 MESH SIZE

SAMPLES 2 & 3



$$V_{N.T.P.} = V_c \cdot \frac{(P+a)}{760} \cdot \frac{25.4}{50} \cdot \frac{273}{273+t}$$

where, V_c = volume of bulb at N.T.P.,

P = burette reading (each division = 1/50 in.)

a = correction for zero reading on burette,

$\frac{25.4}{50}$ = factor for converting burette reading to mms. Hg pressure,

and t = temperature of water bath.

The factor $\frac{V_c \times 25.4 \times 273}{760 \times 50}$ = 1.398 is constant ~~and~~ which is used in all calculations.

a = +9 for lower calibration mark,

= -96 for upper calibration mark.

From dead space curve with helium the dead space volumes corresponding to the pressures (cms. Oil), at which volumes of nitrogen were admitted, were obtained and the volumes of nitrogen adsorbed were calculated by difference as shown in Table (17). The dead space calibration and adsorption graphs for three samples of barytes are drawn in Figs. (58) to (61).

The parking area of an adsorbed molecule, A_o, is assumed to be the same as the cross-section in the interior of the liquefied gas. Secondly, it is assumed that the molecules are spherical in shape.

Hence, $A_o = \left(\frac{M}{PN}\right)^{2/3}$ where M = molecular weight of adsorbate,

P = density of adsorbate in liquefied state,

N = Avogadro's Number $= 6.02 \times 10^{23}$

This gives for adsorbed nitrogen, $A_o = 13.8$ Å^2, and,

for adsorbed nitrous oxide, $A_o = 16.0$ Å^2.

Specimen Calculation.

From Fig. (61) the volume required to form a monolayer on the mineral surface, for sample (2) (120-150 mesh), was found to be 0.283 cc.

Therefore, total number of molecules in monolayer

$$= \frac{0.283}{22400} \times 6.02 \times 10^{23}$$

i.e., total area covered $= 0.283 \times \frac{6.02 \times 10^{23}}{22400} \times 13.8 \times 10^{-16}$ cm^2.

$$= 0.283 \times 37.15 \times 10^{3} \text{ sq. cm.}$$

Hence specific surface $= \frac{0.283 \times 37.15 \times 10^{3}}{27.53}$ sq. cm. per gm.

(weight of barytes used = 27.53)

Discussion of Results.

In table (18) the specific surfaces of three samples of barytes, obtained by adsorption of nitrogen and nitrous oxide, are compared with those of the identical samples by Rigen's method. The values are in the order - nitrogen

adsorption, Rigden's liquid permeability, nitrous oxide adsorption. As is to be expected, the permeability results are lower than those of the gas adsorption, since the latter is considered to represent both the external and internal surfaces. The ratio of these two values which is approximately 1.50 : 1.80 or 1 : 1.2 respectively, is applied later to convert the surface areas from liquid permeability to the "absolute" surface areas.

Four more samples of barytes were taken and their specific surfaces were first determined by means of the Rigden's method. They were then dried at 120°C for three hours and their surfaces re-determined with the Lea and Nurse apparatus. The values obtained were as in the following table:-

TABLE (19)

Mesh.	Specific Surface ($cm.^2/gm.$)		Ratio	Average
	Rigden's (a)	Lea and Nurse (b)	a:b	Ratio
120-150	794.5	632.4	1.26:1	
130-300	750.4	402.7	1.86:1	1.57:1
130-300	865.2	540.3	1.62:1	
130-300	823.7	542.7	1.55:1	

These results show Rigden's method gives values higher than those of the Lea and Nurse method. It has been generally found in the past that the surface area by liquid permeability is lower than that by the air permeability. Rigden's equation includes the correction for 'slip' of air through the channels in the powder bed and the two values

should, therefore, be the same, as found by Rigden. It must, however, be remembered that, in the above comparison, the same apparatus was not used for both methods and, in addition, Rigden's liquid permeabilities were carried out on a bed which had been heavily compacted with a plunger with the result that there is much less segregation of fine and coarse material.

Inter-relation of the above two ratios gave the ratio of the surfaces by gas adsorption and air permeability as 1.2 : 0.637 or 1.9 : 1 approximately. This ratio is used as a correction factor for the surfaces from the air permeability method. This figure is quite reasonable for Cook and Digre (74) obtained a ratio of 1.8 for a similarly relatively non-porous sample of quartz of mesh size 35 to 200 (type of screen not mentioned).

In Table (18) it can be seen that the specific surfaces by nitrogen adsorption are about twice of those with nitrous oxide. A similar observation was made by Macmillan (85) who, using the same method and the same apparatus, found the surface area of a ZnO, Cr_2O_3 catalyst to be 19.75 m^2./gm. by nitrogen adsorption and 4.75 m^2./gm. by nitrous oxide adsorption. This difference may be due to either or both of the two factors:- (a) error in the assumptions made regarding the parking area of nitrous oxide molecule, and (b) the smaller affinity of nitrous oxide for barytes.

The introduction of one oxygen atom into the nitrogen molecule, as in N_2O, could not have caused any great

change in the parking area. The calculated value of A_o, parking area, therefore, is of the right order assuming that A_o for nitrogen molecule is approximately correct.

The second factor is more likely to be the explanation, in which case the formation of an incomplete unimolecular layer is inferred. Although the shape of the isotherms suggests the contrary, i.e., complete unimolecular layer formation, it must be noted that the adsorbent surfaces are, in general, heterogeneous. Adsorption in narrow cracks or pores are higher than those on plane surfaces because of higher heats of adsorption and because the atoms located on the edges and corners of crystals have different degrees of unsaturation from those located on the plane surfaces. Hence, the assumption of a saturated unimolecular layer adsorption is only approximately true and may, in some cases, mean the saturation of just those 'active centres'.

Obviously, in this investigation into the role of the collector, it will be advantageous to know the 'total surface' of the adsorbent coverable by the collector molecules in a unimolecular layer for, then, conclusions may be reached as to how much of this surface is covered by the collector molecules at a known percentage recovery of mineral, knowing, of course, the amount adsorbed. Such a determination is possible by a method employed by Saunders (86). He measured the specific surfaces of calcined and hydrated alumina powders by the adsorption of n-heptoic acid from aqueous solutions, using as a surface tension balance, a

modification of Warren's (87) surface tension apparatus. However, since the nitrogen molecule is relatively smaller than the fatty acid molecule it can give a maximum surface which a collector molecule can be expected to cover. If, therefore, it appears from calculations that the collector has not been adsorbed to the same extent as nitrogen, it does not necessarily mean that a monolayer has not been achieved. It may have, but on the portions of the mineral surface that the fatty acid molecule can reach due to the fact that the fatty acid has a different size and shape from that of the nitrogen molecule.

ADSORPTION OF LOWER FATTY ACIDS ON SILICA, BARYTES & PYRITES.

Chapter X.

Various physical and chemical methods have been employed in the measurement of adsorption from solutions. The physical techniques employed include measurement of refractive index, surface tension, conductivity and radioactivity. The chemical methods naturally comprises both volumetric and gravimetric analyses. Obviously, the choice of a particular method depends upon the nature of the solution and the adsorbent. Where the solution contains strong electrolytes in the absence of interfering ions, the conductivity method can be made use of provided the variation in conductivity with concentration of the solute is appreciable.

The following investigations may be regarded as an attempt to find out the most suitable method for measuring the adsorption of fatty acids from aqueous solutions. Comparatively few adsorption measurements have been made previously in cases of adsorption from aqueous solution on to the mineral surfaces. This is due probably to two difficulties:-

a) ... Owing to the relative insolubility of the reagents being absorbed, it is difficult to have a large enough concentration initially in solution to come within the range of normal methods of analysis in aqueous solution. Again, reagent concentrations in flotation practice are very low (e.g., 0.025 lb. reagent per ton of water is a common value.).

b) ... The quantity adsorbed by unit weight of such minerals

is very much less than that by the more common adsorbents like silica gels, carbon, and activated alumina.

Although the experiments were confined to only three minerals and three physico-chemical methods, they revealed the inherent difficulties met with in this type of work. The first and the most important requisite in an adsorption test is the preparation of pure specimens of the ores. Certain minerals, like silica, are comparatively easy to purify by chemical means while others, like pyrites, can be purified free from impurities only to a limited extent. Undue emphasis may be sometimes laid on the purity of the ore. Attention should be directed to the preservation of the mineral surface as it is found in the natural state. No one can say definitely what sort of changes in the mineral surface may occur in the process of grinding and purification.

Experimental.

Purity of Minerals.

The three minerals used in the experiments on adsorption and flotation were received from the following sources:-

Barytes from Gasswater Mine, Cronberry (Cumnock), Ayrshire, Scotland.

Silica Sand from Loch Aline, Morven, Argyllshire, Scotland.

Pyrites from Messrs. Garroway Ltd. of Glasgow (original source unknown)

The compositions of pyrites as received and purified silica are as given below:-

Mineral	Constituent	Per Cent.
Pyrites	Iron	41.92
	Sulphur	47.50
	Copper	4.21
	Lead	1.52
	Zinc	0.22
	Arsenic	0.38
	Silica and Silicates	4.25
Silica Sand	Silica	95.8
	Aluminium oxide	3.3
	Iron Oxide	0.9

.....

The analytical results of barytes are given in the section on preliminary flotation tests.

Purification of Minerals.

Silica.

About 2 Kgm. of silica sand were taken and washed thoroughly with hot tap water until it was considered to be free from all slimes and soluble impurities. It was then dried and sieved through 50 and 160 mesh B.S.S. screens. The particles between these two sizes were retained and were treated with hot concentrated hydrochloric acid until no iron was detected in the supernatent layer of acid. The acid was

washed away by means of hot distilled water. Finally, grease or oily impurities were removed by washing with ether and absolute alcohol. Half of this sample was dried in an electric oven at 800°C. for 3 hours while the other half was dried in a vacuum steam oven for the same period of time. The two dried specimens were kept under vacuum in desiccators until use.

Pyrites.

1 Kgm. of pyrites, received in the form of chips ranging in size from 1/4 inch to 1/16 inch, was first ground in an iron mortar to pass through 16 B.S.S. mesh. It was then re-ground in the Raymond Mill and sieved through 120 B.S.S. screen. The particles below that size were retained for use. Unlike silica or barytes, pyrites could not be freed from impurities by treatment with acids and it was, therefore, simply washed with hot tap water several times followed by hot distilled water. Petroleum ether and absolute alcohol were used to remove grease and the samples to be tested were dried in a vacuum oven as before.

Barytes.

The purification of barytes is described in the chapter on preliminary flotation tests.

Adsorption Tests.

(1) Acid-Alkali Titration.

An ordinary titration with standard alkali is the most obvious and the simplest method of estimating acid concentrations. A trial experiment showed that the colour

change with the phenolpthalein indicator is not sharp enough to be detectable when the concentration of acid is lower than 0.01N even for formic acid and acetic acids, the two strongest acids in the series. Furthermore, assuming a monomolecular adsorption on the mineral surface, the quantities of lower acids adsorbed will be relatively much smaller than those of the higher members as is evident from a consideration of the molecular weights. Thus taking pyrites, which has the highest surface area per unit weight among the three minerals (see Table (13)), the calculated amount of acid necessary to form a monolayer on the surface, is of the order of 3.0×10^{-4} gm. mols. per 100 gm. of ore; i.e., for the method to be accurate a large weight of mineral must be taken and the initial concentration of the acid in solution must be about 0.001 N or less. The neutralisation method cannot, therefore, be applied in this case.

(2) Conductivity Measurements.

Although the fatty acids are weak electrolytes, it was thought that the conductivities of their solutions in water might be large enough to permit of the differences in conductivities to be measured with reasonable accuracy. Consequently, this method was given a trial.

The conductivity apparatus used was an ordinary Wheatstone Bridge arrangement with the alternating current being supplied by a valve oscillator to which were connected a 2-volt cell and a 60-volt H.T. battery. The three arms of the bridge were represented by the resistances in a Post

Office Box. A simple laboratory type conductivity cell, forming the fourth arm, was placed in a sensitive thermostat. The platinum electrodes, coated with platinum black, were about 2.0 cm. in diameter and were placed horizontally at a distance of about 0.5 cm. apart. A telephone was used to detect the equilibrium point at which the two ratios of resistances became equal. The thermostat was provided with a Beckmann thermometer and temperature of the bath was found to vary by not more than $\pm$ 0.01°C at 25°C. This was taken as satisfactory as the variation in temperature should be not more than 0.2 per cent.. One of the terminals of the P.O. Box was earthed to reduce extraneous sounds in the telephone. The constancy in the volume of liquid taken each time was ensured by a mark on the conductivity cell. For every test the cell with the liquid was allowed to stand in the thermostat for about 10 minutes so as to let the solution attain the temperature of the thermostat.

A preliminary survey of the probable implications reveals that the following two points must be settled before proceeding on to any actual measurements.

They are :-

1) ... In view of the fact that only very small changes in concentration are involved it is essential that the change in conductivity should be appreciably large compared to the corresponding change in concentration.

2) ... The solubility of the adsorbent should be such that it has no effect on the conductivity of the solution or, if it has,

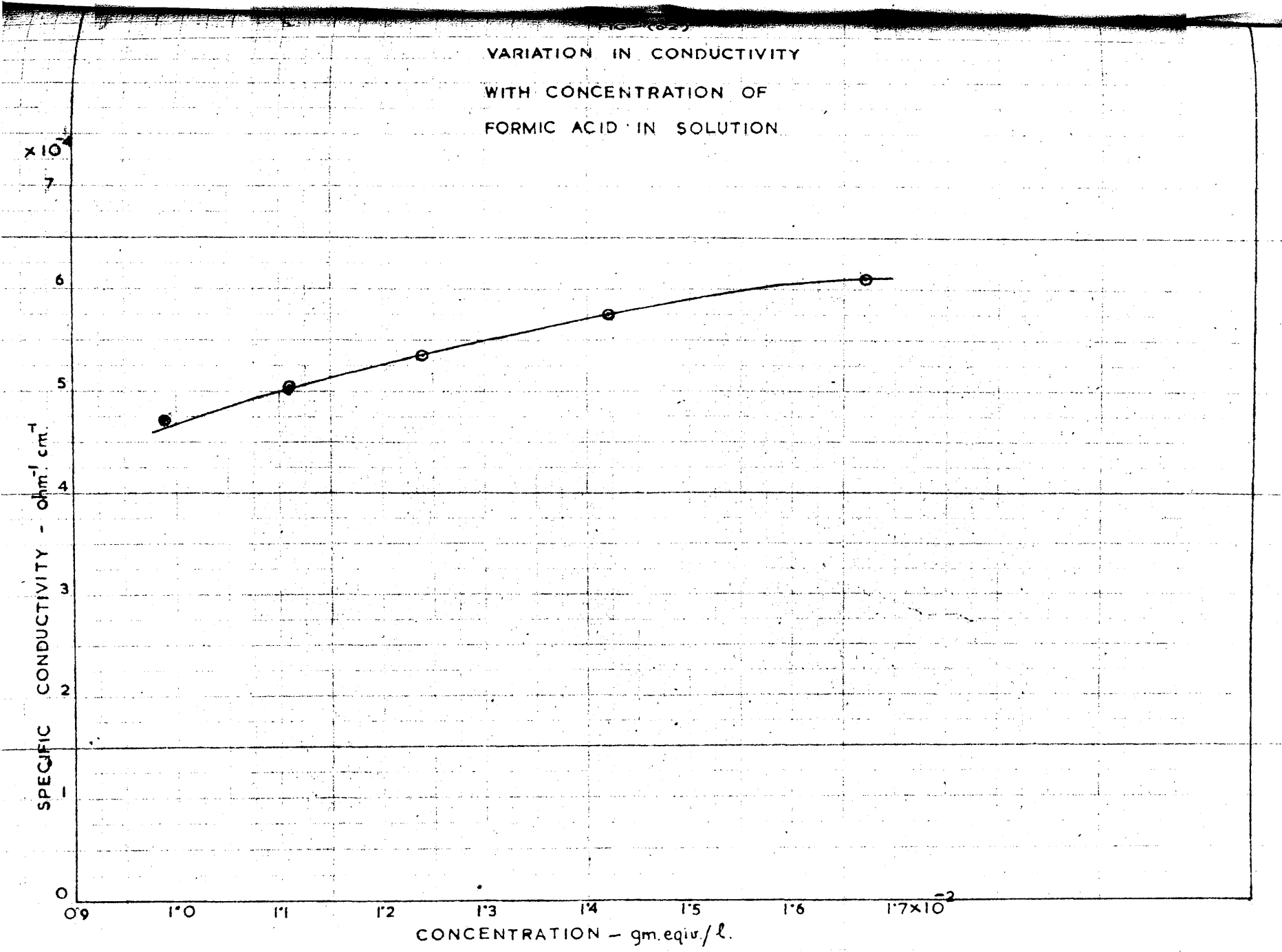
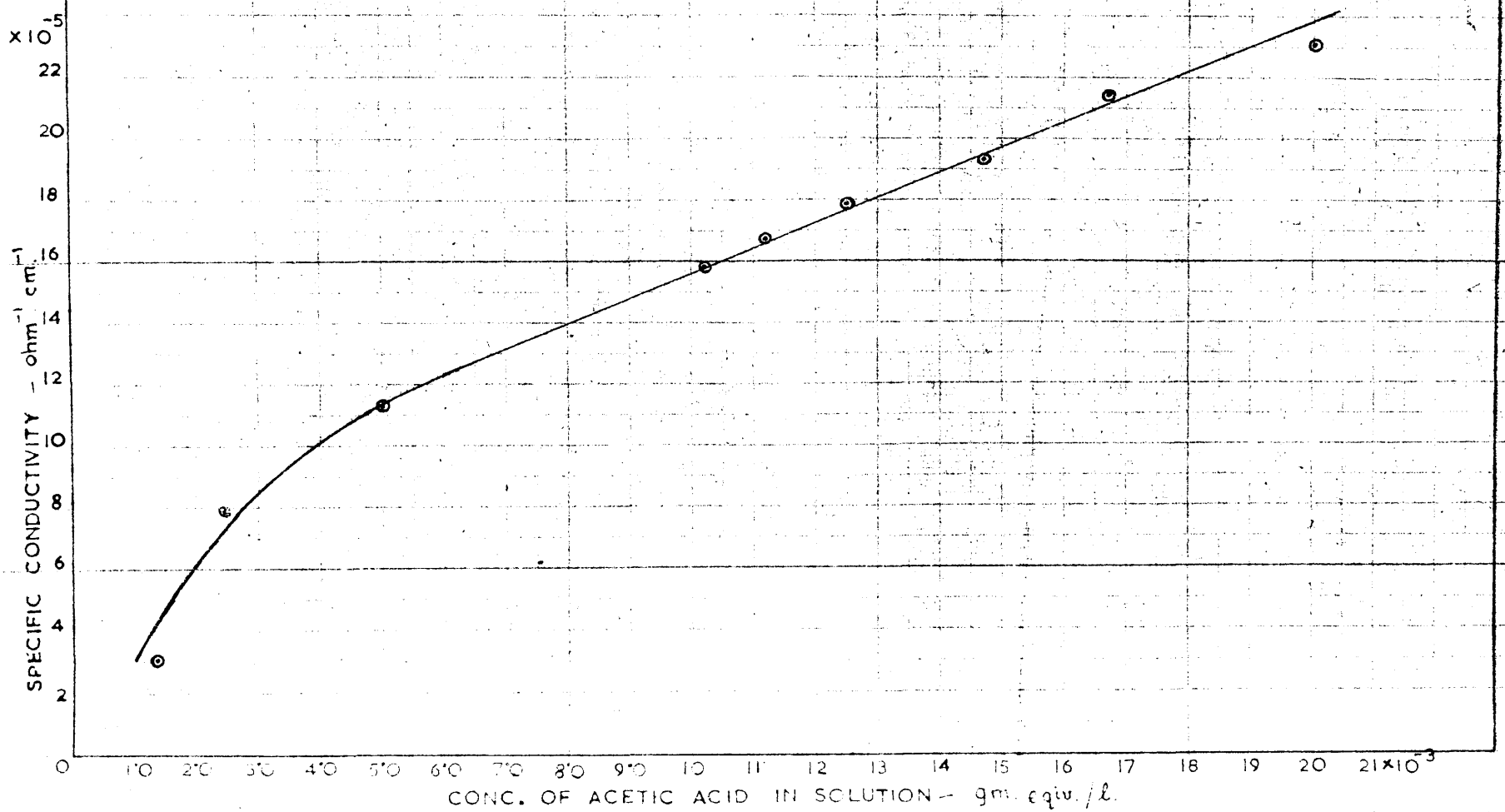

VARIATION IN CONDUCTIVITY
WITH CONCENTRATION OF
FORMIC ACID IN SOLUTION
x 10⁻⁴
7
6
5
4
3
2
1
0
SPECIFIC CONDUCTIVITY - ohm⁻¹ cm⁻¹
0·9
1·0
1·1
1·2
1·3
1·4
1·5
1·6
1·7x10⁻²
CONCENTRATION – gm.equiv./l.

FIG-(63)

VARIATION IN CONDUCTIVITY WITH CONCENTRATION OF ACETIC ACID IN SOLUTION



the effect should be of negligible dimension. Also, the matter would be simplified if the adsorbent's contribution could be accounted for in the total conductivity.

An investigation into the first problem was made by studying the variation in conductivity with concentration of the two first members of the series. These two were chosen because of their comparatively high conductivity and and also because the conductivity values obtained could be easily checked up with the known data in the standard references thus affording the sensitivity of the apparatus to be examined. From the results in Figs.(62) and (63), it can be seen that:-

a) ... In the concentration range investigated for formic acid, i.e., between 0.01 N and 0.02 N, the slope of the curve is too gradual to be of use in measuring concentration change by conductivity. The same will still be true at the lower concentration ranges for the conductivity at 25°C for acid concentrations between 0.12 and 0.001 gm. per litre was given as 2.1×10^{-4} ohm^{-1} $cm.^{-1}$ in the Internation Critical Tables (Vol. (VI) p. 261).

b) ... In the case of acetic acid, the relation between conductivity and concentration is more clearly seen as shown in Fig. (63). Between 0.0083 and 0.02 gm. equivalent per litre an approximate straight line relationship holds. Below 0.0025 gm. equivalent per litre the conductivity falls very rapidly and at the steep part of the curve a decrease in concentration of 0.00125 gm. equivalent per litre gives a decrease in conductivity of 2.83×10^{-5} ohm^{-1} $cm.^{-1}$ which is

TABLE (20)

Variation in Conductivity of Water on Leaving in Contact with Purified Minerals.

No. of Days	Sp. Condty. of Water $ohm^{-1} cm.^{-1}$	Sp. Condty. of Water (ohm^{-1} $cm.^{-1}$) in Contact with		
		Silica	Barytes	Pyrites
0	2.77×10^{-6}	4.51×10^{-6}	2.25×10^{-5}	5.26×10^{-5}
1	3.58×10^{-6}	5.30×10^{-6}	2.87×10^{-5}	10.11×10^{-5}
2	,, ,,	9.02×10^{-6}	3.09×10^{-5}	15.90×10^{-5}
3	,, ,,	,, ,,	3.45×10^{-5}	22.13×10^{-5}
4	,, ,,	,, ,,	3.51×10^{-5}	22.54×10^{-5}
5	,, ,,	,, ,,	,, ,,	,, ,,
6	,, ,,	,, ,,	,, ,,	,, ,,

Table (21)

Acid.	Concⁿ.	Sp.Conductivity of Solution taken at 24 hrs. interval $OHM^{-1}\ cm^{-1}$					Mean Sp. Condtʸ $OHM^{-1}\ cm^{-1}$	Decrease in Sp.Condtʸ $OHM^{-1}\ cm.^{-1}$
		1	2	3	4	5		
Formic	N/50	$7.37x10^{-4}$	$7.35x10^{-4}$	$7.35x10^{-4}$	$7.35x10^{-4}$	$7.35x10^{-4}$	$7.35x10^{-4}$	Nil
Formic + Silica	"	$7.32x10^{-4}$	$7.34x10^{-4}$	$7.38x10^{-4}$	$7.35x10^{-4}$	$7.35x10^{-4}$	$7.35x10^{-4}$	
Acetic	N/50	$2.38x10^{-4}$	$2.36x10^{-4}$	$2.36x10^{-4}$	$2.36x10^{-4}$	$2.36x10^{-4}$	$2.36x10^{-4}$	$5x10^{-6}$
Acetic + Silica	"	$2.30x10^{-4}$	$2.33x10^{-4}$	$2.32x10^{-4}$	$2.30x10^{-4}$	$2.30x10^{-4}$	$2.31x10^{-4}$	
n-Propionic	N/50	$2.22x10^{-4}$	$2.01x10^{-4}$	$2.01x10^{-4}$	$2.06x10^{-4}$	$2.07x10^{-4}$	$2.07x10^{-4}$	$7x10^{-6}$
n-Propionic + Silica	"	$2.12x10^{-4}$	$1.98x10^{-4}$	$1.96x10^{-4}$	$1.99x10^{-4}$	$2.95x10^{-4}$	$2.00x10^{-4}$	
n-Valeric	N/50	$2.06x10^{-4}$	$2.07x10^{-4}$	$2.07x10^{-4}$	$2.07x10^{-4}$	$2.07x10^{-4}$	$2.07x10^{-4}$	$3x10^{-6}$
n-Valeric + Silica	"	$2.00x10^{-4}$	$2.06x10^{-4}$	$2.05x10^{-4}$	$2.04x10^{-4}$	$2.05x10^{-4}$	$2.04x10^{-4}$	
n-Caprylic	N/1300	$3.35x10^{-5}$	$3.65x10^{-5}$	$3.65x10^{-5}$	$3.55x10^{-5}$	$3.60x10^{-5}$	$3.60x10^{-5}$	Nil
n-Caprylic + Silica	"	$3.55x10^{-5}$	$3.70x10^{-5}$	$3.65x10^{-5}$	$3.50x10^{-5}$	$3.60x10^{-5}$	$3.60x10^{-5}$	

equivalent to an increase of almost 1110 ohms in resistance. As the adsorption to be measured is of the order of 3×10^{-4} gm. equivalent per 100 gm. of material, there is a possibility of employing this method provided not less than 100 gm. of adsorbent is used. Beyond 0.00125 gm. equivalent per litre the conductivity approaches the value at infinite dilution as the concentration is reduced and the lower limit of workable concentration is, therefore, fixed at 0.00125 gm. equivalent per litre.

c) ... For the other acids up to n-caprylic acid, corrections will have to be made for the effect due to atmospheric carbon dioxide but a similar relationship between the conductivity and concentration may be expected to hold although the concentration range for n-butyric to n-caprylic acids will be limited by their solubilities in water.

Then to find out whether any interfering ions were liberated by the minerals, 50 gms. of each of purified mineral were shaken with 100 cc. of double distilled water in a ground-glass-stoppered bottles and the conductivity of the resulting water was measured. Shaking the bottle intermittently by hand, the conductivity was taken every 24 hours for a period of 6 days. The readings were as shown in Table (20).

Results.

The results for all the minerals indicate an increase in conductivity of the water to a certain value which remains constant after about 4 days. The increase is the highest

with pyrites and the lowest with silica. It was also found that, in the case of pyrites and barytes, the repeated washing of the purified mineral with distilled water did not help to reduce this effect. On replacing the water that had attained the equilibrium conductivity with a fresh 100 cc. of distilled water, the same behaviour was observed. The reason for this must be the very slow rate of solution of impurities that were included in the crystals of the mineral. This relatively high increase in conductivity made further work with pyrites and barytes almost impossible. To remove all ionic interferences other than those due to the ions from the pure mineral, the particles will need to be reduced to a very fine size before all the impurities could be liberated on purification.

Taking the final conductivity value of water in contact with barytes as 3.587×10^{-6} ohm^{-1} cm^{-1}, the solubility of barytes was found to be 227×10^{-6} gm. equivalent per litre. This is about ten times that of the solubility given in International Critical Tables (Vol. IV, p.256) which is 24.8×10^{-6} gm. equivalent per litre. Hence it may be assumed that the impurities are still present even after a very careful purification process.

A similar solubility calculation was not possible for pyrites owing to the lack of any data on the equivalent conductivity of pyrites at infinite dilution. A qualitative analysis of the water from pyrites showed the presence of ferrous and ferric ions together with those of copper and zinc.

A titration with 0.01 N potassium permanganate solution gave the concentration of ferric ions in solution as approximately 8.2×10^{-4} gm. equ. per litre. The solubility of pyrites from conductivity measurements had been found by Weigel (88) as 48.9×10^{-6} gm. mols. per litre. Apparently, the iron concentration obtained here is much more than what it actually should be according to the solubility data of Weigel.

Another factor to be considered is the rise in conductivity of water which can be attributed to the solution of glass and atmospheric carbon dioxide. As these causes cannot be entirely removed, the 'equilibrium' water that has reached the constant conductivity was used in all the experiments. It may be pointed out, however, that the conductivity of the present water is about three times greater than what it really should be. The conductivity of water, distilled twice over potassium permanganate and in an all-glass apparatus, is stated to be about 0.8×10^{-6} ohm^{-1} $cm.^{-1}$ at 25°C (89).

Adsorption by Silica.

It had already been mentioned that, using acetic acid solution and 50 gms. of a material having a surface area of 200 to 300 $cm.^2$ per gm., a decrease in conductivity of the order of 15×10^{-6} ohm^{-1} $cm.^{-1}$ is obtainable, assuming a monomolecular layer. Thus if silica under 160 mesh, having a surface area of 1051 $cm.^2$ per gm., as determined by Rigden's permeability method (p141), were to be used as adsorbent, the ratio of the change in conductivity due to adsorption, if any,

to that due to the solution of silica and its impurities in water would be about 5:2, in opposite directions. In other words, a decrease in conductivity of about 9.5×10^{-6} ohm^{-1} $cm.^{-1}$ should take place.

Although this value may be admitted as extremely low, it was thought that it would be worth while to carry out some adsorption tests with silica as the results might lead to useful suggestions for further work along this line. The sample of silica that had been ignited to 800°C was used in all the following experiments since it would be free from all organic matter. 50 gm. of dry silica was put into a ground-glass-stoppered bottle together with 200 cc. of the acid solution to be tested, thus making the pulp density the same as that adopted in flotation tests. The mixture was shaken thoroughly for about 3 hours in an agitating machine and then the conductivity of the solution was measured. All the acid solutions were of 0.02 N strength except that of the caprylic acid in which case the concentration was 0.00077 N or 0.1 gm. per litre. A blank experiment was simultaneously carried out with 200 cc. of the acid solution alone in another bottle. Conductivity determinations were continued at 24 hours interval.

Discussion of Results.

From the results in Table (21) the following points emerge:-

1) ... It is difficult to say whether any real adsorption had taken place although some indication in the affirmative was

given by the results for acetic, n-propionic and n-valeric acids. The decreases in conductivity obtained were of the order of the expected value of 9.5×10^{-6} ohm^{-1}, cm^{-1}, i.e., for a monomolecular adsorption.

2) ... From the point of view of direct resistance readings, the corresponding difference between the resistance of the acid solution and that of the same solution over silica ranges from 15 to 38 ohms. As this difference could fall within the limits of experimental error, it seems to support the first conclusion.

3) ... It may be observed that no rise in conductivity occurs with any of the acid solutions in contrast to the case where water alone was used in contact with silica. The significance of this finding is not clearly understood. Silica is one of those substances that can adsorb hydrogen and hydroxyl ions from water. Gaudin and Rizo-Patron (77) assumed that quartz in water is covered with hydrogen and hydroxyl ions in a substantially complete layer and that when the acids are added, the anions take the place of hydroxyl ions. To what extent this exchange of ions occurs in the case of weak acids is not known, but such a state of affairs will amount to the same thing as the adsorption of the two ions of the acid. If this were the case, then the decrease in conductivity due to acid adsorption might have annulled the increase due to emission of ions from silica.

4) ... Since the surface activity increases with the length of the hydrocarbon chain, any adsorption that takes place should

TABLE (22)

Change in pH of Fatty Acid Solutions on Leaving in Contact with Barytes (Under 150 mesh)

Acid	Initial Conc^{n}. g.equ./l.	pH		Increase in pH	Decrease in (H^{+}) Conc^{n}. g.equ./l.
		With Ore	Sol^{n}. Alone		
n-Propionic (a)	0.068	3.17	3.07	0.10	1.75×10^{-4}
(b)		3.15	3.05	0.10	1.80×10^{-4}
n-Butyric (a)	0.057	3.16	3.08	0.08	1.40×10^{-4}
(b)		3.19	3.08	0.11	1.86×10^{-4}
n-Valeric (a)	0.049	3.20	3.12	0.08	1.28×10^{-4}
(b)		3.21	3.12	0.09	1.42×10^{-4}
n-Capric (a)	0.043	3.99	3.65	0.34	1.22×10^{-4}
(b)		3.99	3.65	0.34	1.22×10^{-4}
Conductivity Water (a)	----	6.29	5.91	0.38	7.17×10^{-7}
(b)		6.30	5.93	0.37	6.69×10^{-7}

TABLE (23)

Change in concentration of fatty acid solutions in contact with barytes (under 150 mesh) as determined by Potentiometric Titration.

Soln.	Initial Concn. g.eq./l.	Decrease in Vol. of Std. Baryta rqd. after contact with barytes	Decrease in Concn. of Acid g.eq./l.
m-Propionic Acid (a)	0.068	1.00 cc.	4.72×10^{-4}
(b)		0.25 cc.	1.18×10^{-4}
m-Butyric Acid (a)	0.057	0.625 cc.	2.95×10^{-4}
(b)		1.375 cc.	7.32×10^{-4}
m-Valeric Acid (a)	0.049	0.625 cc.	2.95×10^{-4}
(b)		1.000 cc.	4.72×10^{-4}
m-Capric Acid (a)	0.043	0.625 cc.	2.95×10^{-4}
(b)		0.625 cc.	2.95×10^{-4}

TABLE (24)

Change in pH of Fatty Acid Solutions on Leaving in Contact with Pyrites (under 150 mesh)

Acid	Initial Concn. g.eq./l.	pH		Increase in pH	Decrease in (H^+) conc. g.eq./l.
		With Pyrites	Acid Alone		
Conductivity Water	---	3.86	6.64[a]	2.78[b]	1.44×10^{-4}[c]
m-Propionic Acid (a)	0.068	3.23	2.96	0.33	6.51×10^{-4}
(b)		3.23	2.96	0.33	6.51×10^{-4}
m-Butyric Acid (a)	0.057	3.27	3.00	0.27	6.07×10^{-4}
(b)		3.32	3.00	0.32	6.66×10^{-4}
m-Valeric Acid (a)	0.049	3.28	3.03	0.25	5.53×10^{-4}
(b)		3.26	3.03	0.23	5.28×10^{-4}
n-Caproic Acid (a)	0.043	3.56	3.77	0.21[b]	0.39×10^{-4}
(b)		3.53	3.77	0.24[b]	0.19×10^{-4}

a = Conductivity Water Alone
b = Decrease in pH
c = Increase in Hydrogen Ion Concn.

TABLE (25)

Change in Concentration of Fatty Acid Solutions in Contact with Pyrites (under 150 mesh) as Determined by Potentiometric Titration.

Acid	Initial Concn. g.eq./l.	cc. of Baryta reqd. by 20 cc. of Solution		Estimated Decrease in Vol. of Baryta reqd. - cc.	Estimated Decrease in Acid Concn. g.eq./L.
		With Ore	Soln. Alone		
Conductivity Water	---	4.89	0.01	4.89[a]	13.45×10^{-3}
n-Propionic (a)	0.068	28.98	24.62	0.53	1.46×10^{-3}
(b)		29.16	24.62	0.35	0.96×10^{-3}
n-Butyric (a)	0.057	24.69	20.67	0.87	2.39×10^{-3}
(b)		24.85	20.67	0.71	1.95×10^{-3}
n-Valeric (a)	0.049	21.30	18.75	2.34	6.43×10^{-3}
(b)		21.55	18.75	2.09	5.75×10^{-3}
n-Caproic (a)	0.043	6.28	1.60	0.21	0.58×10^{-3}
(b)		6.05	1.60	0.44	1.21×10^{-3}

a = increase in volume of standard baryta required.

TABLE (26)

Comparison of Theoretical And Experimental Adsorption of Fatty Acids on Barytes and Pyrites.

Acid	Concⁿ. g.eq./l.	Ore	gm.mols. of Acid Adsorbed per gm. of Ore		
			Theoretical	Experimental pH Method	Pot. Titrⁿ.
n-Propionic	0.068	Barytes	1.49×10^{-6}	0.89×10^{-6}	1.26×10^{-6}
n-Butyric	0.057		1.25×10^{-6}	0.81×10^{-6}	1.56×10^{-6}
n-Valeric	0.049		1.34×10^{-6}	0.67×10^{-6}	1.92×10^{-6}
n-Caproic	0.043		1.60×10^{-6}	0.61×10^{-6}	1.47×10^{-6}
n-Propionic	0.068	Pyrites	3.69×10^{-6}	3.26×10^{-6}	6.00×10^{-6}
n-Butyric	0.057		2.59×10^{-6}	3.18×10^{-6}	10.80×10^{-6}
n-Valeric	0.049		4.35×10^{-6}	2.70×10^{-6}	30.25×10^{-6}
n-Caproic	0.043		3.43×10^{-6}	0.14×10^{-6}	4.45×10^{-6}

TABLE (27)

Surface Areas of Powders Used in Adsorption Tests.

Acid	Ore	Mesh Size	Porosity of Bed	Sp. Surface by Rigden's $cm.^2/gm.$	Estimated Sp. Surf. by Gas Adsorption $cm.^2/gm.$
n-Propionic	Barytes	Under 150 B.S.S.	0.281	1529	1835
n-Butyric			0.343	1284	1541
n-Valeric			0.331	1381	1657
n-Caproic			0.335	1648	1978
n-Propionic	Pyrites		0.382	3803	4564
n-Butyric			0.359	2739	3289
n-Valeric			0.383	4472	5366
n-Caproic			0.360	3525	4230

be most clearly indicated by the highest member of the series investigated, viz., n-caprylic acid. The absence of any change in conductivity with this acid means either that the change in conductivity is not a real one with the smaller acids, or more likely that much more sensitive conductivity apparatus and a more elaborate procedure are required to detect the change that actually takes place.

(3) pH measurements and Potentiometric Titrations.

Having found the non-applicability of the conductivity method, the next attempt was made with the pH meter. A Marconi bench type pH meter (TF.511 D) was used for the simultaneous measurement of pH and potentiometric titration.

Barytes and pyrites tested were of size under 150 mesh. 50 gms. of the purified ore and 250 cc. of the fatty acid solution were added to a conical flask closed with a cork wrapped around with silver foil. Occasional agitation was done by hand. The approximate concentrations of the acid solutions were 0.5 per cent. for n-propionic, n-butyric and n-valeric acids, and 0.05 per cent. for n-caproic acid, the actual strengths being determined by titration with standard barytes solution. Two samples of conductivity water were used for barytes and the experiments were conducted in duplicate marked (a) and (b) in Tables (22) to (25). A blank experiment was performed with the ore and water only. As no change was observed immediately on the addition of the solutions the pH determinations and titrations were repeated after a period of 3 days thus allowing any change to come to an

equilibrium.

In potentiometric titration the alkalie solution was first added almost to the neutral point and small additions were then made in steps of 0.05 or 0.02 cc. from a microburette. In the case of pyrites, some difficulty was experienced in taking the E.M.F. reading. It was found later that on allowing the colloidal precipitate of iron hydroxide and other metallic hydroxides to settle, a steady E.M.F. reading could be taken quite easily. From the pH or the titration value, the decrease in concentration of each acid solution is obtained and from this the total decrease in the quantity of acid in 250 ccs. of solution tested is calculated. Table (26) is a summary of the previous tables and a comparison is made between the actual and theoretical adsorptions.

The potentiometric titration method gives directly the change in total acid concentration in solution. In the case of the pH method, however, the assumption, that the decrease in hydrogen ion concentration obtained with each acid is equivalent to the decrease in acid concentration, is based on the following consideration.

Taken as a general case, acetic acid will dissociate in aqueous solution in the following manner.

$$CH_3COOH \quad CH_3COO^- + H^+ \text{ ———————} \quad (1)$$

At equilibrium, $K = \frac{(CH_3COO^-)\,(H^+)}{(CH_3COOH)}$ where K = equilibrium constant,

(CH_3COO^-) = acetate ion concentration,

(H^+) = hydrogen ion concentration,

(CH_3COOH) = undissociated acetic acid concentration.

The adsorption can take place in three possible ways:-

1) ... Neutral acetic acid molecules may be adsorbed in which case the above equilibrium is shifted to the left in the equation (1) with the result that hydrogen ion concentration becomes less.

2) ... The adsorption of acetate ions alone will lead to the dissociation of more acetic acid molecules and consequently there will be an increase in hydrogen ion concentration.

3) ... The adsorption of acetate ions can be accompanied by a simultaneous adsorption of hydrogen ions as counter ions. This will be equivalent to the adsorption of molecular acetic acid as in (1). The pH will increase.

Since, for all acids tested, a decrease in hydrogen ion concentration is indicated, the adsorption of acetate ions alone, as in (2) above, may be ruled out. Of the remaining two mechanisms, (1) and (3), the author is inclined to the view that the acetate ions are adsorbed together with hydrogen ions, as counter ions, for the effect of pH on flotation of barytes, on p. 102 chapter (VII), indicates that the acid anions, and not the neutral molecules, are responsible for collecting action. Hence, it was assumed that the decrease in hydrogen ion concentration is equivalent to the

decrease in acid concentration.

Where iron pyrites was used, a complication arose from its oxidation to iron sulphates and sulphuric acid by the oxygen in water. The resulting increase in hydrogen ion concentration due to the production of sulphuric acid was accounted for in the total hydrogen ion concentration by carrying out a blank experiment with conductivity water alone. The mineral acid will no doubt have an effect on the dissociation of the organic acids.

To estimate the theoretical quantities of acids adsorbed on the particles, assuming a monomolecular layer formation, the surface area of each sample of ore was determined by Rigden's Water Permeability Method, as described in Chapter (IX). The results obtained were converted to the gas adsorption values by multiplying with the factor 1.2. The specific surfaces of the various samples are given in Table (27).

As the adsorption experiments were carried out in duplicate, one 50 gm. lot was used for surface area measurement while the other was kept for flotation tests. The ore was filtered, washed, and dried at 120°C for 4 hours and 25 gms. of this dried ore as taken for each specific surface determination.

Specimen Calculation of Theoretical Adsorption

n-Propionic Acid on Barytes.

Specific Surface of Barytes = 1835 $cm.^2/gm.$

Assume the cross-section of a fatty acid molecule as 20.5 A^2 as

found by compression of insoluble fatty acid films on water.
Avogadro's number = 6.02×10^{23}.

For unimolecular layer formation on 1 gm. of barytes,
the required number of fatty acid molecules = $\frac{1835 \times 10^{16}}{20.5}$

Acid adsorbed per gm. of barytes = $\frac{1835 \times 10^{16}}{20.5 \times 6.02 \times 10^{23}}$ gm. mols.

$= 1.49 \times 10^{-6}$ gm. mols.

Discussion of Results.

From Table (26) it can be seen that, with barytes, the potentiometric method gives results that agree remarkably well with the theoretical values. There are many possible errors in the method such as in the measurement of small volumes of alkali, the measurement of small increments in E.M.F. and the reading of the exact neutral point from the maximum in the ΔE vs. Δv curve. As the acid concentration and not the hydrogen ion concentration is actually concerned in neutralisation, these results seem to indicate a monomolecular adsorption of the acids on the surface of barytes. The very high values obtained in the case of pyrites by this method may be attributed to the occurrence of precipitation reactions at the same time as the acid-alkali neutralisation. Consequently, it may be inferred that where no complications due to other reactions arise, the potentiometric titration method is to be preferred to the pH determination.

It can also be observed that the adsorption calculated from pH of solutions is, in most instances, lower than

the theoretical value and that the decrease in hydrogen ion concentration of the solution becomes smaller as the number of carbon atoms in the molecule increases. The latter may be explained by a consideration of the degree of dissociation of the acids in water. Though the dissociation constants of these four acids do not vary widely from the value 1.30×10^{-5} (90), the degree of dissociation of the acid falls off as the series is ascended. From equation (1) above, it is apparent that the concentration of acid anions ($R.COO^-$) before and after contact with barytes must be known in addition to those of hydrogen ions in order to be able to calculate the actual decrease in acid concentration from a given equilibrium constant. This is difficult to determine owing to the presence of foreign ions in solution.

Flotation Tests.

It was with the object of studying the relation between adsorption and flotation that the following flotation tests were carried out. The remaining 50 gm. of each mineral, were taken and the solution over the solid was decanted off. Another 250 cc. of the same acid solution were added thus making the pulp density the same as before, i.e., 1:5. The flask with the contents was shaken vigorously and the resulting suspension of solid in liquid was poured into the flotation cell up the 75 cc. mark. The flotation cell (A) and the flotation unit are described on p. 60 chapter V. Stirring was done by hand and the same acid solution was fed into the cell from a separating funnel so as to replace the

TABLE (29)

Flotation of Minerals Used in Adsorption Tests

Collector	Conc^{n} gm.eq./l.	Ore	Per Cent. Floated	Conc^{n} of Solid gm./cc.	
				Orgl. Pulp	Overflow
n-Propionic Acid	0.068	Barytes	55.8	0.280	0.021
n-Butyric Acid	0.057		75.3	0.120	0.021
n-Valeric Acid	0.049		82.3	0.205	0.037
n-Caproic Acid	0.043		89.6	0.223	0.041
n-Propionic Acid	0.068	Pyrites	70.9	0.154	0.021
n-Butyric Acid	0.057		85.8	0.159	0.027
n-Valeric Acid	0.049		84.7	0.131	0.043
n-Caproic Acid	0.043		89.0	0.152	0.030

liquid in the overflow. Time of flotation was 5 minutes. The reproducibility of the results is within 5 per cent. Due to the very good collecting action of n-caproic acid solution two identical recovery values were obtained with pyrites on repeating the test. No frother was used since the solutions themselves possess good frothing power. The results are shown in ~~Fig~~ TABLE. (28).

Although the foregoing experiments indicate unimolecular layer formations of the fatty acids on barytes and pyrites, in none of the instances was 100 per cent. recovery obtained. The recoveries obtained here may, perhaps, be the maximum possible for these acids at the completion of unimolecular layers on the surfaces of minerals. Nevertheless, it may be pointed out that, according to later flotation tests (p. 97, chapter VII.), a maximum recovery may be achieved without reaching saturated adsorption at the solid surface.

The acid concentrations being approximately equal, the increase in percentage floated with the increase in number of carbon atoms in the acid molecule supports the general view that the collecting power rises as the homologous series is ascended.

DISCUSSION AND SUGGESTIONS FOR FURTHER WORK.

Chapter XI.

Considering the results obtained in this work, it is at once obvious how difficult it is to generalise about froth flotation theory. The vexed question of ionic adsorption versus neutral molecular adsorption, versus chemical reaction, will continue to remain unsettled if one tries to apply a general theory to every case.

The author has tried to consider the case of the fatty acid molecule and to determine the role of this molecule in froth flotation. A number of the facts obtained are in agreement with those obtained by other workers, viz.,

a) ... That the effective concentrations for the fatty acid collectors are not sufficient to form a complete unimolecular layer on the mineral surface. This is in direct contrast to earlier flotation theory which believed that a complete monolayer of collector must form on a mineral particle before the bubble will attach itself to it. This incomplete layer was found to hold also for the depressant ion, SO_4^{--}, and the activator ion, Ba^{--}.

b) ... That the fatty acids and their soaps are adsorbed physically on the barytes surface, since they can be washed off with alcohol and ether, as shown by the flotation test with the Hallimond Tube (see p. 89). This is supported by by fact that the ratio of the quantity of the higher fatty

acid or soap required for maximum flotation to the quantity of mineral is very much less than the stoichiometric proportion required for the formation of barium salt of the acid.

c) ... Figs. (34) to (36) indicate that recovery is highest at the highest concentration of fatty acid radicle ion, i.e., the anion ($R.COO^-$). This seems to suggest that the adsorption in this case, at any rate, is ionic. Taking this fact together with the results of adsorption tests on page 184, it appears that the adsorption is of the acid anions with the hydrogen ions as counter ions to maintain electrical neutrality The importance of the counter ions in collector attachment has received little attention before this, but must be taken into consideration if one is to obtain a clear picture.

d) ... That the collecting power increases with the increase in the length of the hydrocarbon chain of the fatty acid or soap molecule up to a certain limit which is 16 carbon atoms in the case of fatty acids and 14 carbon atoms for soaps.

e) ... That although the fatty acids and soaps possess both collecting and frothing ability, the lower members exhibit good frothing property and poor collecting action while the higher members have good collecting power and low froth stabilities at least in the concentration ranges investigated.

Even though the depressing action of the ferric ions on flotation of barytes has been found previously, systematic investigation into the actual role played by the ferric ions has been lacking up to now. Positive adsorption of these metallic ions even in the presence of a collector

coating on the barytes surface is indicated by the experiments carried out. The adsorption of ferric ions, however, seems to be independent of the adsorption of the collector ions. Thus, less ferric ions are adsorbed on the mineral surface where a coating of laurate ions is already present. It should be noted that the collector coating is that which is formed at maximum recovery since flotation tests on the samples tested before iron adsorption give nearly 100 per cent. recovery.

In Figs. (51) and (52) it can be seen that ferric ion adsorption in the presence of laurate ion coating follows the same trend as that without the coating. Such regular decrease in ferric ions in solution with increase in equilibrium concentration would not be possible if reaction were to take place between the collector ions and ferric ions. The author is, therefore, led to the view that the barytes surface is made hydrophilic by the adsorption of ferric ions in the presence of the collector.

Then, the treatment of the depressing effect of ferric ions by means of the triangular diagrams is an entirely new approach to these flotation systems containing three effective ions in solution. From these diagrams, the contribution of each ion to the total effect can be seen clearly.

Of the anions considered, the carbonate ion has no effect as such on the flotation of barytes with sodium

laurate. This indirectly proves that the atmospheric carbon dioxide has no influence on the flotation.

On the experimental side, a new flotation cell was developed together with the necessary technique which,it is hoped,will prove useful to later investigators.

Surface area determinations were done with a view to finding out the surface available to the collector in the tests. Three methods were employed but a new method is needed not only to handle powders of widely different particle sizes but also to work with small quantities of powders varying from about 1 gm. to about 15 gms.. In the laboratory flotation tests, where the weight of each sample tested does not usually exceed 50 gms., such a method would allow the surface areas of both the recovery and the tailings to be measured.

A problem of paramount importance is the measurement of adsorption of collectors on the mineral surfaces. It has been shown that the pH method and the potentiometric method cannot be applied in the case of sparingly soluble collectors such as higher fatty acids and soaps. A surface tension method might be used. Saunders' (86) modification of Warren's (87) maximum bubble pressure apparatus could be tried. With this simple apparatus, Saunder measured the adsorption of n-heptoic acid from aqueous solution by calcined and hydrated alumina powders. Care will, however, have to be taken that the mineral tested does not give off interfering ions in solution. The analytical method of Barr, Oliver, and Stubbings (91) is also

interesting. These investigators determined the surface active anions and cations by direct titration with methylene blue and bromophenol blue respectively in organic solvents. At the end-point, the blue colour of the complex formed between the methylene blue and the surface active compound is discharged.

Further suggestions that one might make for extending this study are:-

1) ... The study of the effect of the characteristics of the flotation cell on flotation and the comparison of different flotation cells.

2) ... The study of the effect of temperature variation on flotation, and in particular flotation at high temperatures (e.g., at 60°C.). For this purpose the flotation cell (B) Fig. (14), fitted with an outside thermostatic jacket, will be useful.

3) ... The effect of the introduction of the side chains or double and treble bonds in the straight-chain fatty acids on flotation may be studied using the technique applied in this work.

4) ... Although investigations regarding the adsorption of metallic ions on the surfaces of minerals from aqueous solutions have increased recently, more systematic work along this line is needed. The adsorption could be studied in aqueous solutions with and without the collector and the results for pure synthetic ore and the natural ore could be compared. In this connection, work on the solubilities of heavy metal salts

of the higher fatty acids could be of value in understanding the activation and depression caused by the metallic ions in the presence of these acids as collectors.

Many such subjects of interest for further study can be cited particularly as the science of flotation is still in its youth. Research on froth flotation embraces several aspects of inorganic, physical and organic chemistry. The fruits of flotation research have been reaped not only in the field of mineral dressing but also in may previously unexpected places. For example, the separation of ergot from rye, detergency, and filtration are just three instances where the results of such research have been applied successfully. Thus, further advances in froth flotation will be of significance to both pure and applied science.

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